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Study on catalysts of selective reduction of NO_x using hydrocarbons for natural gas engines

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Abstract

The effect of water on selective catalytic reduction of NO_x using hydrocarbons (HC-SCR) on Cu- and Co-ZSM-5 was investigated. Co-ZSM-5 showed a higher HC-SCR activity and selectivity using C_3H_8 than Cu-ZSM-5 at temperatures above 400°C in the presence of water. On Co-ZSM-5, C_3H_8 oxidation by O_2 was slow and severely inhibited by water due to Co-ZSM-5's poor ability to adsorb O_2 dissociatively, and the capacity for NO adsorption was large enough to supplement the poor NO oxidation activity. These adsorption properties are therefore considered to contribute to the high activity and selectivity observed on Co-ZSM-5. Among the Co-based catalysts, Co-Beta showed higher HC-SCR activity and was more durable than Co-ZSM-5.

Keywords: Reduction; NO_x; Natural gas engines; Cu-ZSM-5 catalyst; Co-zeolite catalyst

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1. Introduction

Lean burn natural gas engines are considered as advanced power source for cogeneration systems because their power generation efficiency is much greater than stoichiometric gas engines. However, due to the lacking of any convenient method to reduce nitrogen oxides (NO_x) from the exhaust containing excess oxygen, their use has not been wide spread. Recently, it has been reported that NO_x is selectively reduced by hydrocarbons (HC), even in the presence of excess oxygen, on metal ion-exchanged zeolite [1–5], H-form zeolite [6] and γ-Al_2O_3 [7]. Among them, Cu ion-exchanged ZSM-5 (Cu-ZSM-5) is reportedly the most efficient catalyst for selective catalytic reduction of NO_x using hydrocarbons (HC-SCR). However, light alkanes, the only available HC for lean burn gas engines, are not so effective for HC-SCR as alkenes on Cu-ZSM-5 [8], and the selectivity of NO_x reduction by light alkanes is quite low from a viewpoint of the application for lean burn gas engines. Further, it has been observed that HC-SCR is inhibited by the presence of water vapor [3]. Therefore, it is considered that Cu-ZSM-5 cannot be used to remove NO_x from lean burn gas engines. Quite recently, HC-SCR using CH_4 has been reported on Co ion-exchanged ZSM-5 (Co-ZSM-5) [9,10], Ga ion-exchanged ZSM-5 (Ga-ZSM-5) [11] and In ion-exchanged ZSM-5 [12]. However, the activity of NO_x reduction by CH_4 on these catalysts is

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also suppressed by the presence of water [12–14].

In this paper, HC-SCR by C_3H_8, involved in natural gas supplied as city gas, was examined under the condition of lean burn gas engine exhaust on two representative catalysts: Cu-ZSM-5 and Co-ZSM-5. The reaction stage suppressed by water was investigated to find a way to improve the catalytic activity in the presence of water. Moreover, improvement of catalyst was carried out based on the investigation, and the initial activity and durability of the improved catalysts are reported.

2. Experimental

Cu-ZSM-5 and Co-ZSM-5 were prepared from NH_4-ZSM-5 ($SiO_2/Al_2O_3 = 50$) by ion exchange using an aqueous solution of metal acetate for 10–18 h at 25°C for Cu and at 60°C for Co. The ion exchange procedure was repeated twice for Cu and 6 times for Co. Other Co-zeolites were prepared in a similar way except for the number of times of ion exchange. The ion-exchanged zeolites were washed, dried and pressed into tablet followed by crushing into particles of 1–2 mm, and then calcined in air at 500°C. The ion exchange rate is calculated from the content of Cu or Co assuming that one metal ion (2+) is exchanged with two NH_4^+. In this paper, for example, Cu-ZSM-5 (50, 111%) represents an ion-exchanged ZSM-5 of SiO_2/Al_2O_3 molar ratio = 50 with Cu ion exchange level of 111%. Co/Al_2O_3 was prepared by impregnation as a reference.

Catalytic activity was measured in a fixed bed flow reactor made of stainless steel (catalyst bed 14 mmϕ×25 mm). The test gas was generated from He-balanced standard gas by mass flow controllers, and water was added by a pump through a gasifier to the test gas before it entered the reactor. The gas composition at the outlet of the reactor at stationary state was analyzed by a gas chromatograph and a chemiluminescence NO_x analyzer with an NO_2 converter. NO_x and C_3H_8 conversions were defined as (evolved N_2)/(inlet NO) and (inlet C_3H_8-outlet C_3H_8)/(inlet C_3H_8), respectively.

Temperature programmed desorption (TPD) was carried out using an ultra high vacuum system as described elsewhere [14,15].

3. Results and discussion

3.1. Differences in the effect of water vapor on HC-SCR on Cu-ZSM-5 and Co-ZSM-5

The catalytic activities of SCR by C_3H_8 under the conditions of lean burn natural gas engine exhaust in the presence and absence of water are shown in Fig. 1 for Cu-ZSM-5 and Co-ZSM-5. On Cu-ZSM-5 (a), both NO_x and C_3H_8 conversions were totally suppressed by water at 300°C.

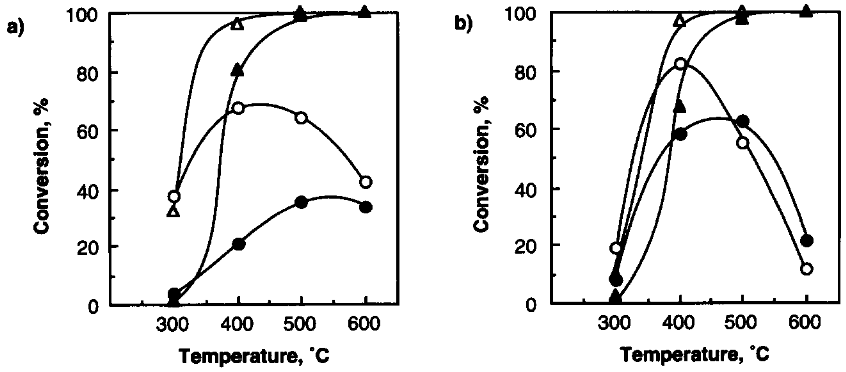

Fig. 1. Effect of water vapor on activity of HC-SCR by C_3H_8 on Cu- and Co-ZSM-5. Catalysts: (a) Cu-ZSM-5 (50, 106%), (b) Co-ZSM-5 (50, 111%). Reaction conditions: NO = 500 ppm, C_3H_8 = 1000 ppm, O_2 = 10%, CO_2 = 6%, CO = 1000 ppm, H_2 = 660 ppm, GHSV = 30 000 h^{-1}, H_2O = 0% (○, △), or H_2O = 9% (●, ▲), He balance. ○, ●: conversion of NO into N_2; △, ▲: conversion of C_3H_8.

Table 1
The influence of the water on the amount of NO Adsorption derived from TPD

Catalyst	Clean		H_2O-preexposed			
	Desorbed NO, N ml/g	TPD peak temperature, °C	Desorbed NO, N ml/g	TPD peak temperature, °C	Desorbed H_2O, a.u.	TPD peak temperature, °C
Cu-ZSM-5 (50, 111%)	0.047	94	0.027	83	153	93
Co-ZSM-5 (50, 117%)	0.067	83	0.039	75	100	89
Co-Beta (22,80%)	0.113	83	0.062	69	127	69

Exposure: NO = ca. 260 L, H_2O = ca. 1200 L (1 L = 1.33×10^{-4} Pa·s), temperature = ca. 30°C. Sample weight = ca. 15 mg, heating rate = 100°C/min.

At 400°C, whereas C_3H_8 conversion reached 80%, NO_x conversion was below 20%. The selectivity of NO_x reduction, represented by (NO_x Conv.)/(C_3H_8 Conv.) was clearly decreased by water at temperatures above 400°C. That is, water not only suppresses the low temperature activity of HC-SCR but also decreases the selectivity of NO_x reduction at a higher temperature on Cu-ZSM-5. On the other hand, on Co-ZSM-5 (b), low temperature activity was slightly inhibited by water, while the selectivity of NO_x reduction was not affected. As a result, the temperature region of HC-SCR shifted a little higher, and Co-ZSM-5 shows higher NO_x conversion than Cu-ZSM-5 around 400°C under the conditions of lean burn gas engine exhaust. This difference between Cu- and Co-ZSM-5 suggests that the reaction stages inhibited by water are different on Co-ZSM-5 from those on Cu-ZSM-5, therefore, which reaction stage is influenced by water was investigated.

First, the influence of water on NO adsorption was examined using TPD because it has been reported that Cu- and Co-ZSM-5 adsorb large amounts of NO [16], which may contribute to their high HC-SCR activity. The amounts of desorbed NO from clean and water-preexposed Cu- and Co-ZSM-5 are shown in Table 1. Both on Cu- and Co-ZSM-5, NO adsorption was inhibited by water preadsorption to a similar extent, though the absolute amount of NO adsorption was larger on Co-ZSM-5 than on Cu-ZSM-5. As for the amount of C_3H_8 adsorption, which is not considered to be directly related to the selectivity of NO_x reduction, there was no actual change by water preadsorption on either Cu- or Co-ZSM-5, which is quite different from the case of Ga-ZSM-5 [14].

It has been reported that NO oxidation into NO_2 is the first reaction step of HC-SCR on many kind of catalysts, such as γ-Al_2O_3 [17], Cu-ZSM-5 [18–20], and Co-ZSM-5 [21]. Fig. 2 shows the effect of water on the reaction: $NO + 1/2O_2 \leftrightarrows NO_2$ on Cu- and Co-ZSM-5. On Cu-ZSM-5 (a), the reaction reached equilibrium at temperatures above 400°C in the absence of water, and proceeded near to equilibrium at 400°C even in the presence of water. On the other hand, the activity of the reaction on Co-ZSM-5 (b) was lower than on Cu-ZSM-5, further, the reaction was suppressed by water to a higher degree than on Cu-ZSM-5. However, the fact of the stronger suppression of NO oxidation by water on Co-ZSM-5 means that competitive C_3H_8 oxidation by O_2 must be also suppressed by water on Co-ZSM-5 to maintain the selectivity of NO_x reduction.

Fig. 3 shows how C_3H_8 conversions on Cu- and Co-ZSM-5 were changed by water when the inlet gas composition was NO-C_3H_8-O_2, NO_2-C_3H_8-O_2 or C_3H_8-O_2. In the absence of water, on Cu-ZSM-5 (a), the presence of NO_x increased C_3H_8 conversion, but the difference of C_3H_8 conversions in the presence and absence of NO_x was very small. Therefore, a simple combustion reaction of C_3H_8 by O_2 is fairly fast on Cu-ZSM-5. There is

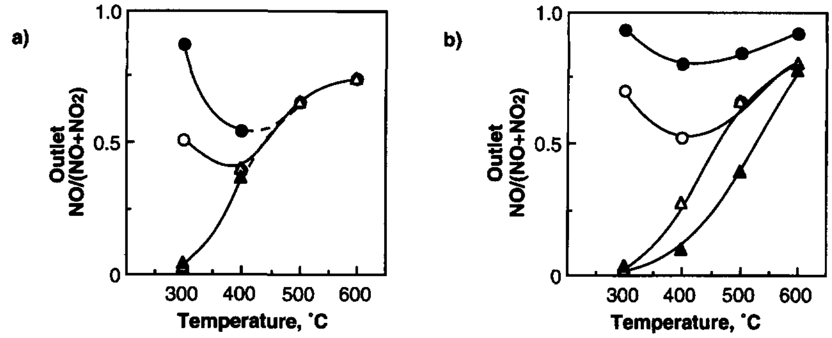

Fig. 2. Effect of water vapor on NO oxidation on Cu- and Co-ZSM-5. Catalysts: the same as Fig. 1. Reaction condition: GHSV = 30 000 h^{-1}, O_2 = 10%, H_2O = 9% (closed symbol) or 0% (open symbol), inlet NO_x = 1000 ppm (○, ●: NO = 1000 ppm or △, ▲: NO_2 = 1000 ppm).

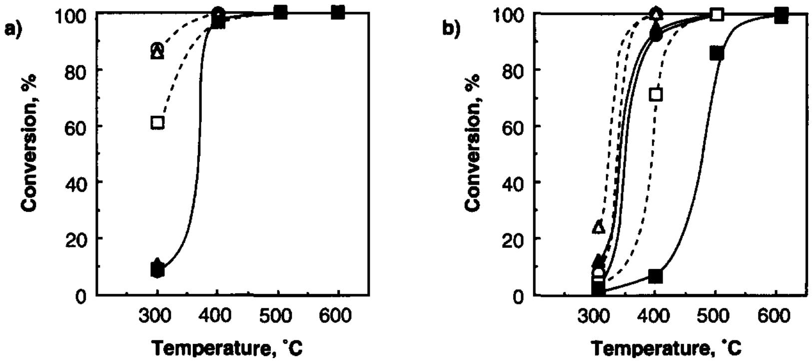

Fig. 3. Effect of water vapor on C_3H_8 conversion on Cu- and Co-ZSM-5. Catalysts: the same as Fig. 1. Reaction conditions: GHSV = 30 000 h^{-1}, O_2 = 10%, H_2O = 9% (closed symbol) or 0% (open symbol), C_3H_8 = 1000 ppm, NO_x = 1000 ppm (○, ●: NO = 1000 ppm or △, ▲: NO_2 = 1000 ppm) or 0 ppm (□, ■).

no difference in C_3H_8 conversion in the case of NO and NO_2 as the inlet NO_x. This is because the equilibrium reaction between NO and NO_2 is very rapid on Cu-ZSM-5, as shown in Fig. 2. C_3H_8 conversion on Cu-ZSM-5 was not decreased by water at temperatures above 400°C and was independent of the existence of NO_x, although the C_3H_8 conversion was slightly reduced by water at 300°C. This means that C_3H_8 oxidation by O_2 is less sensitive to water than HC-SCR on Cu-ZSM-5 under this condition. On the contrary, on Co-ZSM-5 (b), the difference of C_3H_8 conversion in the presence and absence of NO_x was larger than Cu-ZSM-5 under water-free condition. This suggests that the rate of C_3H_8 oxidation by O_2 is much less than Cu-ZSM-5. Further, at 300°C, C_3H_8 conversion in the case of NO_2 exceeds that of NO and so the reaction rate of NO oxidation also influences the C_3H_8 conversion. C_3H_8 oxidation by O_2 was considerably suppressed by the presence of water, while C_3H_8 conversion in the presence of NO_x was slightly decreased by water. Accordingly, the difference of C_3H_8 conversion in the presence and absence of NO_x remained sufficient to show the high selectivity of NO_x reduction even in the presence of water.

Thus, it can be concluded that the reactions of NO oxidation and C_3H_8 oxidation by O_2 are slower and inhibited by water more severely on Co-ZSM-5 than on Cu-ZSM-5. Since these reactions result from oxidation by O_2, this suggests a difference in the ability to activate oxygen on Cu- and Co-ZSM-5. Fig. 4 shows TPD profiles of O_2 from Cu- and Co-ZSM-5. The amount of O_2 desorbed at temperatures above 400°C, due to the dissociatively adsorbed oxygen species, is large on Cu-ZSM-5 and quite small on Co-ZSM-5. Further, the amount was not decreased by the preadsorption of water on Cu-ZSM-5. Such dissociatively adsorbed oxygen might contribute to accelerating HC oxidation and to reducing the selectivity of the NO_x reduction in HC-SCR [15].

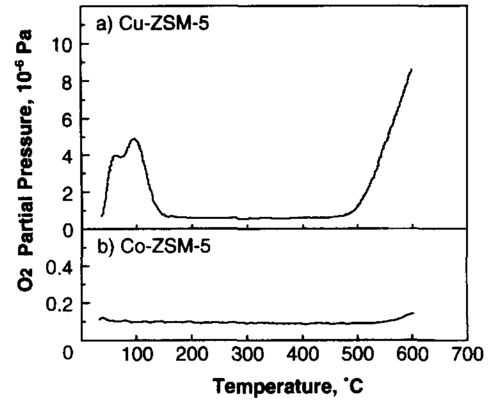

Fig. 4. TPD spectra of O_2 from Cu- and Co-ZSM-5. Catalysts: (a) Cu-ZSM-5 (50, 104%), (b) Co-ZSM-5 (50, 117%). Exposure = ca. 300 L at ca. 30°C. Sample weight = 10.3 mg (a), 15.4 mg (b). Heating rate = 100°C/min.

Therefore, it can be concluded that neither NO oxidation nor C_3H_8 oxidation are inhibited by water on Cu-ZSM-5 because dissociatively adsorbed oxygen amply exists on Cu-ZSM-5 even in the presence of water.

From these results, if the amount of adsorbed species is proportionally related to the concentration of the intermediate adsorbate state for HC-SCR and the main reaction path is the same for both Cu- and Co-ZSM-5, the difference between Cu- and Co-ZSM-5 may be explained as follows. Although many reaction mechanisms have been proposed for HC-SCR, a scheme shown in Fig. 5 may be considered as the most acceptable main reaction path [17,20,21] except for the oxidation steps (2) and (5). If an oxidation without dissociatively adsorbed oxygen is the main path on Co-ZSM-5 and the oxidation is severely inhibited by water, the present results are all consistent, although the detailed mechanism of the inhibition by water is still unclear. On Cu-ZSM-5, the high reaction rate of (5) due to dissociatively adsorbed oxygen is not suppressed by water while NO adsorption (1) is inhibited, and so, the selectivity of NO_x reduction decreases. On the other hand, on Co-ZSM-5, NO oxidation (2), possibly the rate limiting stage, is inhibited by water but C_3H_8 oxidation (5) is also severely suppressed, and as a result, the selectivity does not decrease. The influence of water on NO adsorption is not considered to effect the selectivity so much as on Cu-ZSM-5 because NO oxidation is the rate limiting stage due to the severe inhibition of water on Co-ZSM-5, and because the amount of NO adsorption is slightly larger than Cu-ZSM-5.

The desirable characteristics of a good catalyst for HC-SCR are large NO adsorption capacity (1), high NO oxidation rate (2), large HC adsorption capacity (3), high reaction rate for NO_x reduction (4) and low HC oxidation rate (5). However, poor dissociative adsorption of O_2 not only contributes to a low HC oxidation rate but also causes a low NO oxidation rate. A low HC oxidation rate is essential to obtain high selectivity of HC-SCR, and so, large NO and HC adsorption capacities even in the presence of water are desired to supplement the poor NO oxidation activity. From the present results, Co-ZSM-5 has the desired characteristics, and accordingly showed a higher HC-SCR activity under the conditions of lean burn gas engine exhaust.

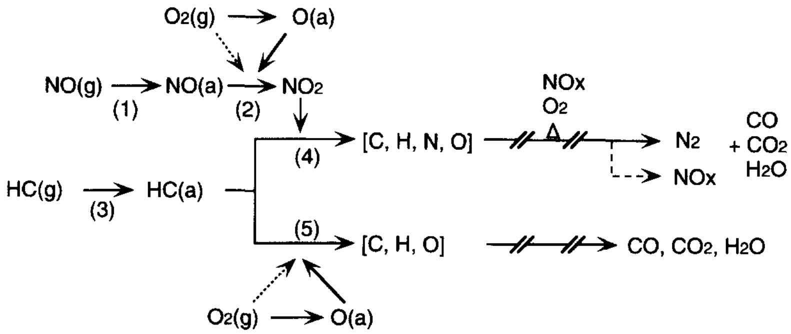

Fig. 5. Hypothetical reaction scheme of HC-SCR.

3.2. Improvements of Co ion-exchanged zeolite catalysts

The characteristics of Co-ZSM-5 are considered to originate in the properties of Co; therefore, several Co-based catalysts have been explored. The catalytic activities of HC-SCR by C_3H_8 are shown in Table 2 for representative Co ion-exchanged zeolites as well as Co/Al_2O_3. The data in Table 2 cannot be directly compared because many parameters of the catalysts are different, however, the best result is listed for each zeolite among samples having various SiO_2/Al_2O_3 ratio, ion exchange rate, etc. Co-Y showed almost no HC-SCR activity. The activity of Co-FER was low, which might be attributed to the low ion exchange rate. Co-MOR had a higher activity at 400°C than Cu-ZSM-5. Co/Al_2O_3 showed a high activity at 500°C, but inefficient at 400°C, exhibiting a clear contrast to zeolite-based catalysts. Although the activity on Co-ZSM-5 was very high among Co-zeolite catalysts, Co-Beta showed much higher NO_x conversion over a wider temperature range. It is not due to high Co content because Co-Beta (44, 110%) also showed similar activity.

Table 2
HC-SCR activity using propane on Co-based catalysts

Catalyst	SiO_2/Al_2O_3 ratio	Co content, wt.-%	NO_x (C_3H_8) conversion, %			
			300°C	400°C	500°C	600°C
Co-Y	4.8	8.2 (64)[a]	0.0 (0.0)	0.0 (1.9)	3.9 (51.2)	– (–)
Co-Ferrierite	16.0	1.29 (28)[a]	0.9 (5.5)	1.7 (7.2)	18.2 (36.0)	– (–)
Co-MOR	11.2	5.2 (74)[a]	11.0 (2.5)	54.2 (91.1)	35.4 (100.0)	– (–)
Co-ZSM-5	50.0	2.0 (111)[a]	9.1 (2.4)	65.6 (76.4)	65.0 (97.8)	10.1 (100.0)
Co-Beta	22.3	3.0 (80)[a]	0.0 (4.2)	83.7 (94.7)	86.0 (99.8)	54.7 (100.0)
Co-Beta	44.1	2.22 (110)[a]	– (–)	83.4 (99.8)	73.4 (100.0)	– (–)
Co/Al_2O_3	–	1.0	4.7 (6.2)	19.9 (8.4)	75.4 (61.4)	18.1 (100.0)

Reaction conditions: NO = 500 ppm, C_3H_8 = 1000 ppm, O_2 = 10%, CO_2 = 6%, CO = 1000 ppm, H_2 = 660 ppm, H_2O = 9%, GHSV = 15 000 h^{-1}.

[a] The values in parentheses are ion exchange rates.

The characteristics of the HC-SCR activity on Co-Beta are high activity at low temperatures and high selectivity of NO_x reduction at high temperatures. Furthermore, the decrease in activity due to the presence of water was lower than Co-ZSM-5, though the results are not shown. The adsorption properties of NO, C_3H_8 and O_2 on Co-Beta were investigated using TPD. The amount of NO adsorption on Co-Beta was larger than on Co-ZSM-5 as shown in Table 1, although the amount was also reduced by water on Co-Beta to an similar extent to Co-ZSM-5. The amount of adsorbed C_3H_8 on Co-Beta was comparable to that on Co-ZSM-5. Therefore, it is considered that Co-Beta shows higher activity at low temperatures partly because Co-Beta adsorbs larger amounts of NO than Co-ZSM-5. On the other hand, the desorption of O_2 from O_2-exposed Co-Beta was no longer observed even at temperatures above 550°C, at which a trace amount of desorbed O_2 was observed on Co-ZSM-5 as shown in Fig. 4b. Therefore, Co-Beta definitely has no ability to dissociatively adsorb oxygen detectable by TPD. This is considered to be the reason that the selectivity of NO_x reduction does not decrease even at high temperatures leading to high NO_x conversion on Co-Beta over a wide temperature range.

However, the little influence of water on HC-SCR on Co-Beta cannot be explained by the above-mentioned adsorption properties because the NO oxidation rate was slower than on Co-ZSM-5 due to the lack of dissociatively adsorbed oxygen. It may be suggested that the large pore size, two dimensional straight channels and three dimensional pore network of Beta zeolite enable the easy diffusion of reactants, products, inhibitors such as water and inert molecules. Certainly, such a pore structure may be an advantage to maintain high dispersion of Co.

3.3. The durability of Co ion-exchanged zeolite catalysts

It is known that zeolites are generally unstable in the presence of water vapor at high tempera-

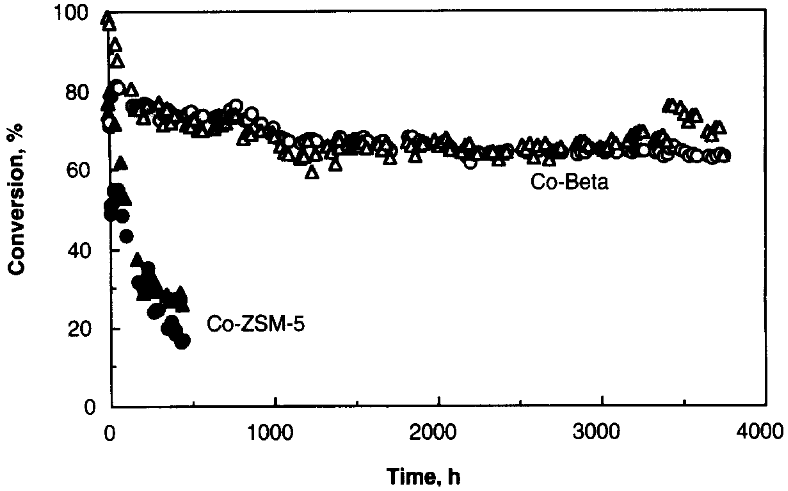

Fig. 6. Durability of activity of HC-SCR by C_3H_8 on Co-Beta and Co-ZSM-5. Catalyst: Co-Beta (16.3, 98%, open symbol), Co-ZSM-5 (50, 106%, closed symbol). Reaction condition: NO = 150 ppm, C_3H_8 = 500 ppm, O_2 = 10%, H_2O = 9%, SO_2 = 0.3 ppm, CO_2 = 6%, CH_4 = 1000 ppm, CO = 500 ppm, H_2 = 250 ppm, He balance, T = 400°C, GHSV = 15 000 h^{-1}. (○, ●: NO_x conversion, △, ▲: C_3H_8 conversion).

tures, and, therefore, the durability of zeolite based catalysts must be established under the condition of actual exhaust containing water vapor for practical use. Moreover, as the authors have reported, Cu-ZSM-5 does not have sufficient durability at 500°C under the conditions of lean burn gas engine exhaust, because Cu aggregates to form CuO clusters even though the zeolite framework structure does not change [22].

Fig. 6 shows the results of durability tests of HC-SCR by C_3H_8 for Co-ZSM-5 and Co-Beta using a model gas containing 0.3 ppm of SO_2, corresponding to the concentration in the exhaust of lean burn gas engines. The figure clearly demonstrates that Co-Beta exhibited stable HC-SCR activity for 4000 h except for an experimental error around 1000 h, while Co-ZSM-5 does not have sufficient durability at 400°C. The HC-SCR activity of Co-MOR decreased more rapidly than Co-ZSM-5. Although Co-ZSM-5 and Co-MOR showed a high HC-SCR initial activity, the activities are not high enough to maintain practically high conversions. In contrast, Co-Beta not only has excellent initial activity but sufficient durability under the conditions of lean burn gas engine exhaust. Cu ion-exchanged Beta (Cu-Beta) was also prepared, but showed activity comparable to that of Cu-ZSM-5 under the conditions of Fig. 1, and also showed a tendency to deteriorate similar to that of Cu-ZSM-5. Therefore, the durability of Co-Beta is considered to originate in Co's stable dispersion due to Co's own properties as well as Beta's specific pore structure.

Finally, a durability test using the actual exhaust from a lean burn gas engine was performed, and the durability of Co-Beta has been established for more than 1000 h. Thus, Co-Beta is very promising for practical use as a NO_x reduction catalyst for lean burn gas engines.

4. Conclusion

Co-ZSM-5 showed a higher activity of HC-SCR by C_3H_8 than Cu-ZSM-5 at temperatures above 400°C in the presence of water, because the selectivity of NO_x reduction was not decreased by the presence of water. In contrast to Cu-ZSM-5, only a trace amount of dissociatively adsorbed oxygen was observed on Co-ZSM-5, and as a result, C_3H_8 oxidation by O_2 was slower and more severely inhibited by water than on Cu-ZSM-5. Although NO oxidation activity was also quite low due to Co-ZSM-5's poor ability to adsorb O_2 dissociatively, the capacity of NO adsorption was sufficient to supplement the poor NO oxidation activity. Therefore, these adsorption properties are considered to contribute to the high activity and selectivity of NO_x reduction on Co-ZSM-5.

Among Co-based catalysts, Co-Beta with its larger NO adsorption capacity, no dissociative oxygen adsorption ability and better pore structure for diffusion than Co-ZSM-5 showed higher initial HC-SCR activity as well as excellent durability.

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