Catalysis Letters 61 (1999) 77–82

Enhancement of activity for NO removal of MFI-type H-Co-silicate by high-temperature pretreatment

Dangsawai Tapanee[a], Praserthdam Piyasan[a,*] and Tomoyuki Inui[b]

[a] *Department of Chemical Engineering, Chulalongkorn University, 10330 Thailand*
E-mail: tapanee@rocketmail.com; fengpps@chulkn.car.chula.ac.th
[b] *Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*

Received 14 April 1998; accepted 17 June 1999

The effect of high-temperature pretreatment in the presence of steam on NO conversion of protonated cobalt-incorporated silicate having MFI structure (H-Co-silicate) and copper-ion-exchanged MFI-type zeolite (Cu/H-ZSM-5) was studied. The activity of Cu/H-ZSM-5 decreased with an increase of pretreatment temperature. In contrast with Cu/H-ZSM-5, the activity of H-Co-silicate for NO removal increased with the pretreatment temperature. As for H-Co-silicate, the pretreatment at 1000 °C was the optimum condition to enhance the conversion that was four times higher than that without pretreatment. The destruction of framework and loss of cobalt species were not observed after the pretreatment. Some parts of cobalt species migrated from the framework and became active sites that enhance the activity for NO removal.

Keywords: high-temperature pretreatment, steam, Co-silicate, NO removal

1. Introduction

Removal of nitric oxide using hydrocarbons as the reductants has been studied in the presence of excess oxygen in the past decade. Among the catalysts, zeolites and their related materials were extensively used for this purpose. Copper-ion-exchanged H-ZSM-5 (Cu/H-ZSM-5) is well known to be an effective catalyst for removal of nitric oxide in the presence of excess oxygen [1,2]. Unfortunately, since Cu/H-ZSM-5 is easily deactivated at high temperature (>800 °C) in the presence of steam which possibly occurred in practical use [3–6], many researchers try to find a new catalyst having high performance for nitric oxide removal even in the presence of steam. Armor et al. [7] and Budi et al. [8] found that cobalt-ion-exchanged H-ZSM-5 catalyst (Co/H-ZSM-5) can suffer in the condition of steam and temperature less than 800 °C. Nevertheless, owing to the ease of sintering of the exchanged metal component and dislocation of the alumina in the framework under high, severe condition, the decrement of activity on nitric oxide conversion occurred. On the other hand, protonated cobalt-incorporated silicate having MFI structure (H-Co-silicate) is proposed to be a powerful catalyst that can be stable against the deterioration under severe condition at high temperature even with water [9,11]. It was found that the loss of activity of metallosilicates for nitric oxide removal was much smaller than that of ion-exchanged zeolites after high-temperature calcination. Moreover, in previous studies it was found that the pretreatment affected the activity of H-Co-silicate for nitric oxide elimination [12]. As referred above, the pretreatment of H-Co-silicate is worthy for improvement of nitric oxide removal. Accordingly, the objective of this study is to find out the optimum pretreatment condition enhancing the activity of H-Co-silicate for nitric oxide removal. We also describe the activity for nitric oxide removal observed here comparing with similar studies on Cu/H-ZSM-5.

2. Experimental

2.1. Catalyst

Co-silicate MFI-type zeolite was prepared by the rapid crystallization method [13]. The charged Si/Co atomic ratio of Co silicate was set at 20. As-synthesized crystals were washed, dried and heated at the temperature of 540 °C for 3.5 h in an air stream. Subsequently, they were ion-exchanged twice with an NH_4NO_3 aqueous solution, followed by the calcination at 540 °C for 3.5 h in air. They are designated as H-Co-silicate. For copper-ion-exchanged zeolite, ZSM-5 zeolite was synthesized by the same method as mentioned above. The charged Si/Al atomic ratio was set at 50. After transformation into H type, it was ion-exchanged using a copper acetate solution, followed by the same approach to gain 200% Cu-ion-exchanged HZSM-5. The catalysts were pretreated and carried out for reaction tests.

2.2. Characterization

In order to measure the crystallinity of the samples, X-ray diffraction patterns were obtained by an X-ray refractometer, Shimadzu XD-D1, with Ni-filtered Cu Kα ra-

---

[*] To whom correspondence should be addressed.

diation. BET surface area and the bulk metal composition of the catalysts were measured by Shimadzu Flow Sorb II 2300 and inductively coupled plasma analysis (ICP Shimadzu ICPS-1000 III), respectively. Diffuse reflectance UV-visible spectra were analyzed by a Shimadzu MPS-2000 spectrometer installed with a multi-purpose reflectometry attachment, RTA-2000, using $BaSO_4$ as a reflectance standard. Electron spin resonance spectra were recorded with an X-band Jeol JES-RE2X spectrometer equipped with a microwave power 1 mW at liquid-nitrogen temperature. *In situ* FTIR spectra analyzed by a Nicolet model Impact 400 were applied for acidity measurement of the sample using pyridine as a probe molecule. Additionally, ^{29}Si MAS NMR analysis was adopted using a Jeol 270 SGX at 53.7 MHz. For TPR measurement, a 0.2 g portion of catalyst was reduced in a 5% H_2/Ar stream from room temperature to 800 °C at the heating rate of 10 °C/min. The concentration of hydrogen in the effluent gas was recorded by a TCD gas chromatograph after water vapor removing by a cold trap at methanol–dry ice temperature.

2.3. Pretreatment condition

For studying the effect of pretreatment on nitric oxide removal, H-Co-silicate and Cu/H-ZSM-5 were calcined in the temperature range from 600 to 1,100 °C in an atmosphere of He. The catalysts were heated with a constant heating rate of 10 °C/min from room temperature to 600 °C and of 1.67 °C/min from 600 to 1,100 °C using an electric oven. The catalyst was then kept at the desired temperature for 30 min and then cooled down to room temperature.

2.4. Catalytic reaction

The catalytic reaction was carried out using an ordinary flow microreactor under atmospheric pressure. To avoid pressure drop during the reaction test, the powder catalyst was tabletted, crushed, and sieved into 12–22 mesh. In order to investigate the activity for NO removal, the catalyst was heated in a He flow to 600 °C and maintained at that temperature for 30 min. Then a feed gas composed of 1,000 ppm NO, 1,000 ppm n-C_8H_{18}, 2% O_2, 10% H_2O balanced with He was allowed to flow with a GHSV of 30,000 h^{-1}. The reactants and products were analyzed by gas chromatographs (Chrompack, Micro GC CP 2002 with MS-5A and Porapak Q column) after the steady state of catalytic activity. To ensure the steady state of catalytic activity, NO and n-octane conversions were analyzed every 5 min after introducing the feed gas. The catalytic activities for nitric oxide reduction and n-octane combustion were investigated as the amount of N_2 and carbon oxides (CO_x; $CO_2 + CO$) produced, respectively. Reaction tests were undertaken every 50 °C with diminishing from 600 to 200 °C, followed by the same procedure as mentioned above.

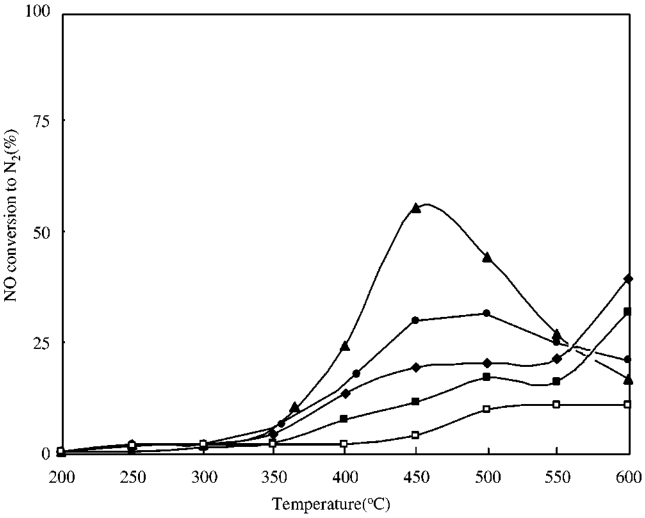

Figure 1. The effect of pretreatment of H-Co-silicate on NO conversion to N_2 in the presence of steam. (■) Without pretreatment; (◆) pretreated at 800 °C; (●) pretreated at 900 °C; (▲) pretreated at 1,000 °C; (□) pretreated at 1,100 °C. Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O_2 2%, H_2O 10%, He balance, GHSV 30,000 h^{-1}.

3. Results and discussion

3.1. The effect of pretreatment of the catalyst on its catalytic performance

As demonstrated in figure 1, the activity of H-Co-silicate for NO conversion increased with an increase of the pretreatment temperature except for the temperature of 1,100 °C. From these results, the temperature of 450 °C is chosen to be the optimum reaction temperature to investigate the performance of H-Co-silicate for NO removal. Observation of NO conversion to N_2 at 450 °C indicated that the order of the activity for NO to N_2 conversion was as follows: $1{,}100 \ll 800 < 900 < 1{,}000$ °C. Without pretreatment, the NO conversion to N_2 on H-Co-silicate was only 15% at 450 °C. Interestingly, the conversion to N_2 after pretreatment at 1,000 °C increased up to 60%. This conversion is approximately four times larger than that without pretreatment. In contrast with H-Co-silicate, the NO conversion to N_2 of Cu/HZSM-5 decreases with pretreatment temperature as illustrated in figure 2. As compared with NO conversion to N_2 for Cu/HZSM-5 without pretreatment, NO conversion to N_2 after pretreatment at 1,000 °C decreases remarkably more than three times at 450 °C. This is supported by [14]. Therefore, it is elucidated that for H-Co-silicate the pretreatment at high temperature is valuable for enhancement of NO conversion to N_2.

3.2. The effect of pretreatment on structure of catalysts

XRD patterns of H-Co-silicates and Cu/H-ZSM-5s are shown in figures 3 and 4, respectively. After pretreatment, H-Co-silicate maintains the MFI structure even at 1,100 °C. However, the intensity of X-ray diffraction lines of H-Co-silicate after pretreatment at 1,100 °C is lower

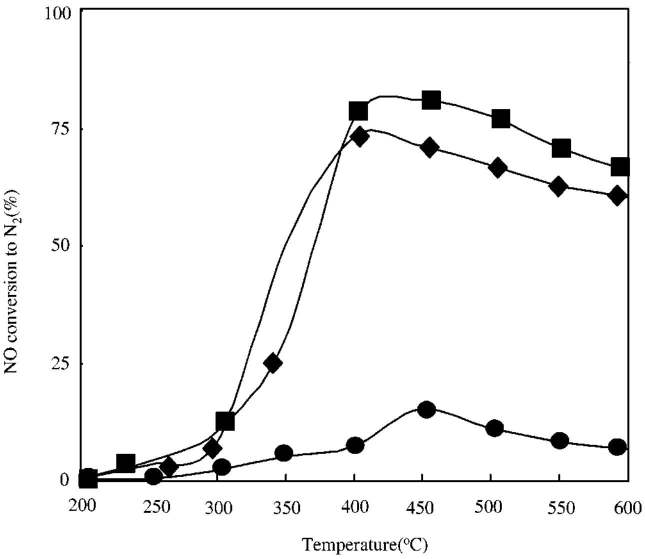

Figure 2. The effect of pretreatment of Cu/H-ZSM-5 on NO conversion to N_2 in the presence of steam. (■) Without pretreatment; (♦) pretreated at 800 °C; (●) pretreated at 1,000 °C. Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O_2 2%, H_2O 10%, He balance, GHSV 30,000 h^{-1}.

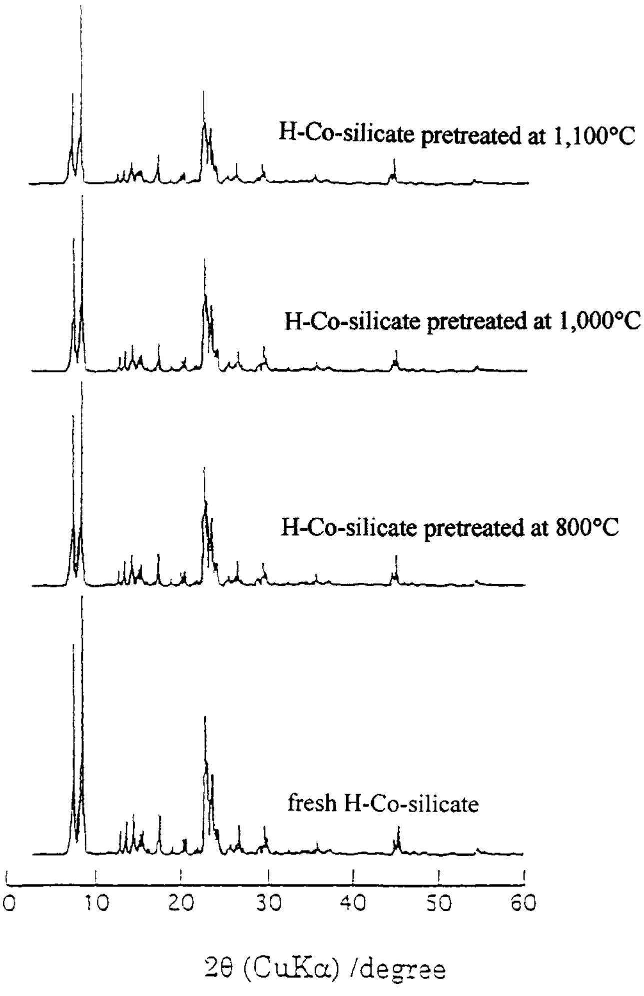

Figure 3. XRD patterns of H-Co-silicate after pretreatment.

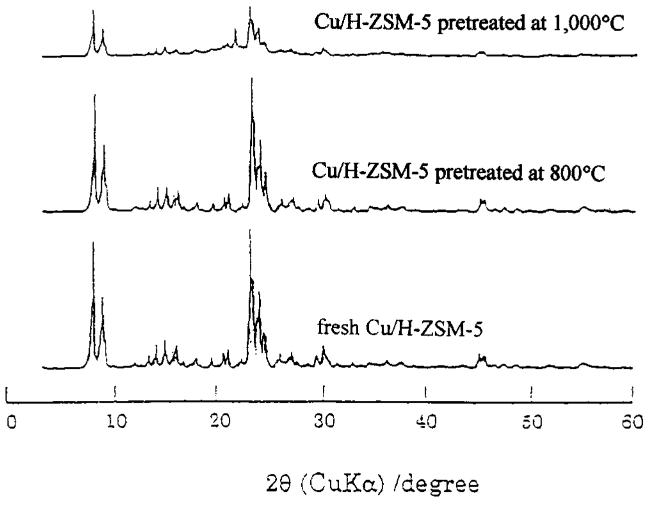

Figure 4. XRD patterns of Cu/H-ZSM-5 after pretreatment.

Table 1
Change in BET surface area and bulk composition of H-Co-silicates and Cu/H-ZSM-5s.

Sample	Pretreatment temperature (°C)	BET surface area (m^2/g-cat)	Si/Me atomic ratio
H-Co-silicate	without pretreatment	350	257
	800	345	257
	1,000	400	258
	1,100	355	258
Cu/H-ZSM-5	without pretreatment	360	51
	800	300	54
	1,000	120	56
	1,100	2[a]	–

[a] Drawn from the data in [25].

than that without pretreatment. It can be indicated that, after pretreatment at 1,100 °C, H-Co-silicate has lower crystallinity causing the loss of performance for NO removal. But for Cu/H-ZSM-5, the XRD pattern after pretreatment at 1,000 °C changes visibly, compared with that without pretreatment. The intensity of identified diffraction lines at around 23.1, 8.03, 23.94° 2θ which are ascribed to silicon oxides as cristobalite form appeared after pretreatment at 1,000 °C. Therefore, it means that MFI-type structure of Cu/H-ZSM-5 is destroyed by the high-temperature pretreatment, as supported by a previous paper [11]. The surface area of the catalysts is summarized in table 1. As compared with fresh H-Co-silicate, the BET surface area of H-Co-silicate after pretreatment is not changed differently. On the other hand, in comparison with the BET surface area of fresh Cu/H-ZSM-5, the BET surface area of Cu/H-ZSM-5 after pretreatment is decreased with pretreatment, especially at 1,000 °C. From these data, it can be concluded that H-Co-silicate can maintain the MFI structure in high, severe pretreatment condition without any change of framework. Additionally, the chemical composition of the bulk for H-Co-silicates was measured by ICP analysis. From ICP data, although Si/Co obtained differed from a ratio setting due to the difficulty of cobalt incorporation in the framework, the amount of cobalt after pretreatment did not decrease even at 1,100 °C. As a result, cobalt species exhibit the thermal stability in H-Co-silicate. In order to investigate the framework and non-framework Co in H-Co-silicate, UV-VIS spectra of H-Co-silicate without and with pretreatment at 1,000 °C were recorded. As illustrated in figure 5, UV-VIS spectra of H-Co-silicates show the adsorption band between 500 and 650 nm assigned to tetrahedral Co(II) and at around 350 nm assigned to tetrahedral Co(III) [15,16]. After pretreatment at 1,000 °C, the absorption peak at 350 nm is

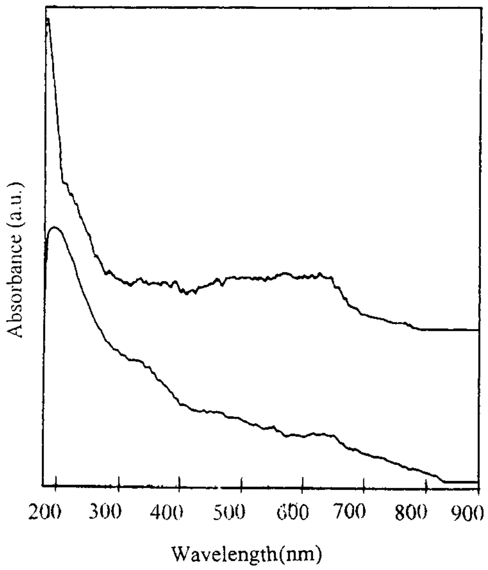

Figure 5. Electron absorption spectra of samples. Top: fresh H-Co-silicate; bottom: H-Co-silicate pretreated at 1,000 °C.

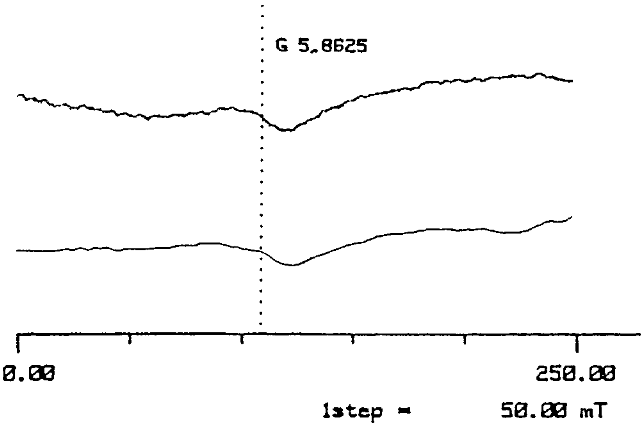

Figure 6. ESR spectra of samples. Top: fresh H-Co-silicate; bottom: H-Co-silicate pretreated at 1,000 °C.

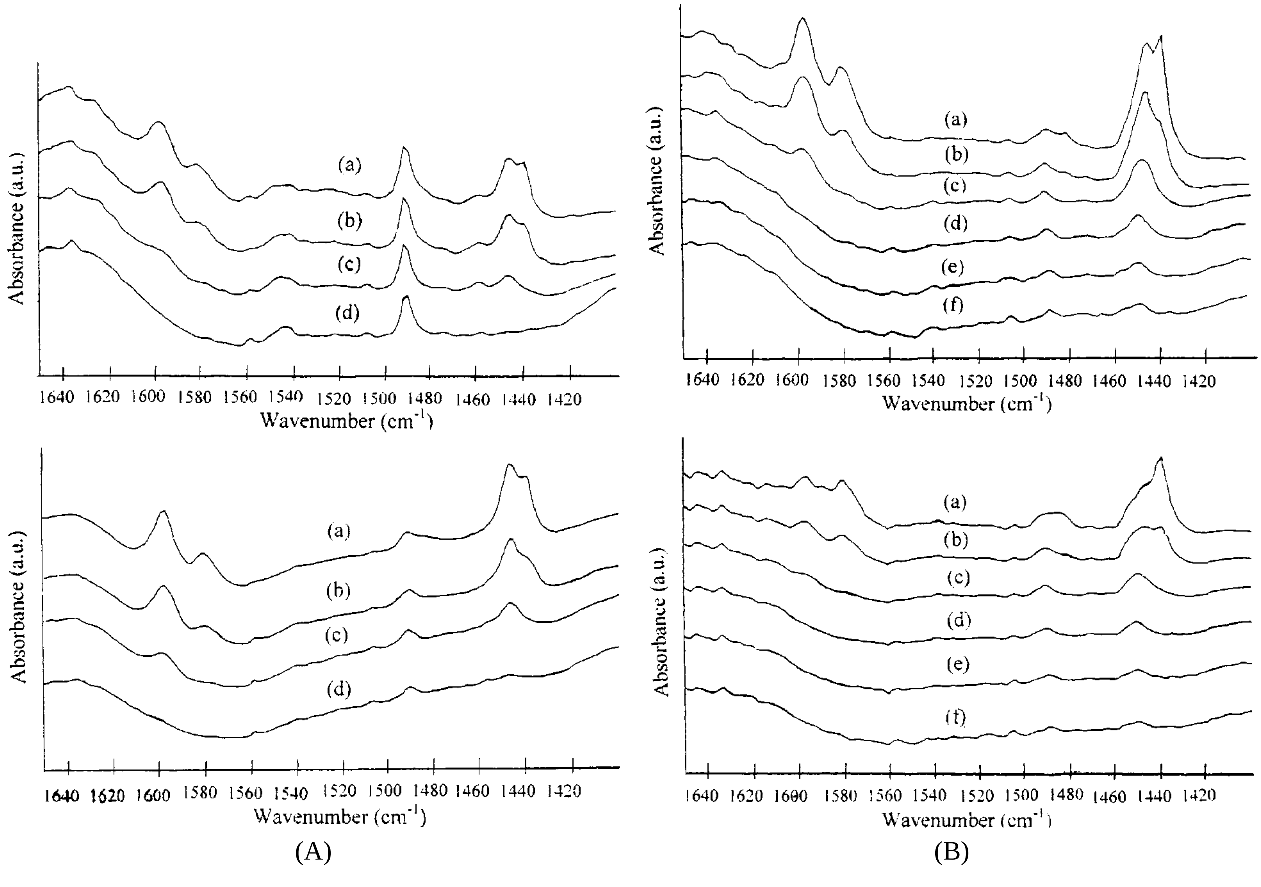

Figure 7. (A) *In situ* FT-IR spectra of pyridine adsorbed on silicalites. Top: fresh silicalite; bottom: silicalite pretreated at 1,000 °C; (a) at room temperature; (b) at 50 °C; (c) at 100 °C; (d) at 150 °C. (B) *In situ* FT-IR spectra of pyridine adsorbed on H-Co-silicates. Top: fresh H-Co-silicate; bottom: H-Co-silicate pretreated at 1,000 °C; (a) at room temperature; (b) at 50 °C; (c) at 100 °C; (d) at 150 °C; (e) at 200 °C; (f) at 250 °C.

broadened, and charge transfer is observed while the intensity of a remnant at 500–650 nm becomes flat and even still remains. It can be suggested that, after pretreatment at 1,000 °C, some part of tetrahedral Co(II) is changed to Co(III). Furthermore, cobalt oxides clusters are also observed on H-Co-silicate pretreated at 1,000 °C similar to the study of Kagawa et al. [12]. Figure 6 shows ESR spectra of H-Co-silicate with and without pretreatment. Both spectra show the signals at $g \approx 5.86$ assigned to high-spin Co^{2+} [16–18]. The shape and intensity of signals obtained from pretreated H-Co-silicate at 1,000 °C infinitesimally change from that of H-Co-silicate without pretreatment, indicating that a part of Co aggregates and affects the coordination state of high-spin Co^{2+}. Furthermore, the acidity of catalysts analyzed by the amount of pyridine adsorbed on acidic solids is shown in figure 7. It can be summarized that silicalite has no Lewis acidity even before pretreatment at 1,000 °C. As for H-Co-silicate after pretreatment at 1,000 °C, the intensity of the band at around 1440–1465 cm^{-1} which can be used to determine Lewis acidity [19] is lower than that of H-Co-silicate without pretreatment. This also indicates that a part of tetrahedral Co moved out from the framework structure. And as shown in figure 8 for ^{29}Si NMR analysis data of H-Co-silicate with and without pretreatment, it shows a signal at approximately -111 and -115 ppm assigned to Si $Q^4(4Si)$. Moreover, the shape of line signal of pretreated H-Co-silicate at 1,000 °C was roughly similar to that of standard silicalite indicating that MFI structure was maintained even after pretreatment at 1,000 °C. Moreover, H_2 TPR was carried out to analyze the cobalt species in H-Co-silicate and depicted in figure 9. From H_2 TPR data, in addition to the consistence with a hydrogen uptake peak of H-Co-silicate without pretreatment at around 700 °C, a new hydrogen uptake peak is observed at about 500 °C for H-Co-silicate pretreated at 1,000 °C. It can be indicated the presence of a part of cobalt oxides [20,21] highly dispersed on H-Co-silicate after pretreatment at 1,000 °C. As the results mentioned above, it can be concluded that, after pretreatment at 1,000 °C, some part of tetrahedral Co(II) in the framework changed to Co(III) and formed cobalt oxide species that enhance the activity of NO removal. The possible appearance is the migration of a part of cobalt in the framework to the extraframework, which is supported

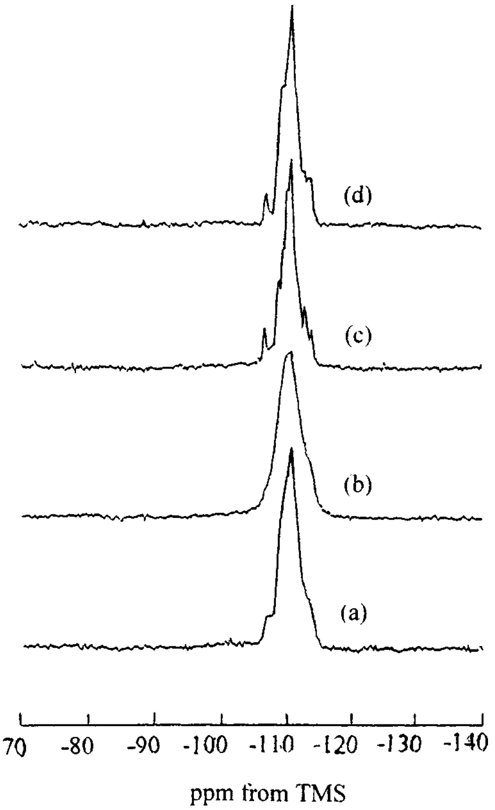

Figure 8. The change of ^{29}Si NMR spectra of (a) fresh H-Co-silicate, (b) H-Co-silicate pretreated at 800 °C, (c) H-Co-silicate pretreated at 1,000 °C, and (d) fresh silicalite.

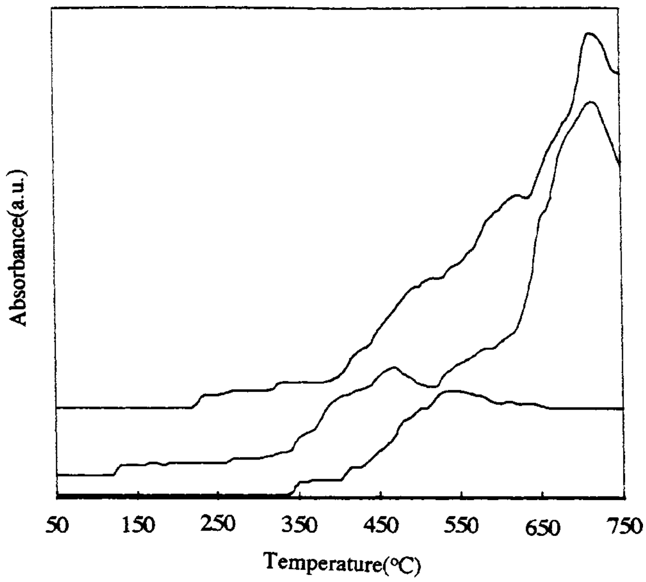

Figure 9. Temperature reduction profiles of catalysts. From top to bottom: fresh H-Co-silicate, H-Co-silicate pretreated at 1,000 °C, fresh silicalite.

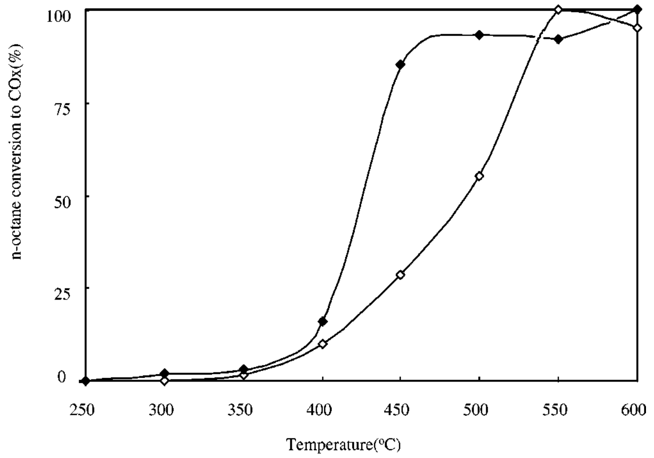

Figure 10. n-octane combustion conversion of H-Co-silicate. (◇) Without pretreatment; (◆) pretreated at 1,000 °C. Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O_2 2%, H_2O 10%, He balance, GHSV 30,000 h^{-1}.

by the study of Kagawa et al. [12]. To elucidate the enhancement of activity of H-Co-silicate after pretreatment at 1,000 °C, the n-octane conversion to carbon oxides (CO_x) is shown in figure 10. It is observed that, by using the pretreatment at 1,000 °C, the activity for n-octane combustion of H-Co-silicate increased distinguishingly. Compared with H-Co-silicate without pretreatment, the light-off temperature of H-Co-silicate after pretreatment at 1,000 °C is shifted to lower temperature. For these results and previous studies [12,22–24], it can be proposed that after pretreatment at 1,000 °C some parts of cobalt educed from the framework and became dispersed cobalt oxide species. In addition to cobalt incorporated in the framework, dispersedly educed cobalt species enhance the combustion activity and encourage the NO conversion to N_2.

4. Conclusions

The pretreatment at high-temperature condition can enhance the activity of H-Co-silicate for nitric oxide elimination. For H-Co-silicate, the pretreatment at 1,000 °C is the optimum condition to improve the performance for NO removal effectively. The activity for NO conversion of H-Co-silicate after pretreatment at 1,000 °C was about four times higher than that without pretreatment. H-Co-silicate exhibits high structural stability of the framework during pretreatment even at the severe condition of 1,000 °C. The effect of thermal treatment at 1,000 °C is to change the state of cobalt species that enhance the activity for nitric oxide removal.

Acknowledgement

We acknowledge the financial support of National Science and Technology Development Agency (NSTDA). We also wish to thank T. Takeguchi, Y. Ono, S. Iwamoto, and M. Inoue for MAS-NMR study, ICP measurement and cooperation in this study.

References

[1] M. Iwamoto, H. Yahiro, K. Tanda, N. Mizuno, Y. Mine and S. Kagawa, J. Phys. Chem. 95 (1991) 3727.

[2] M. Iwamoto, H. Yahiro, N. Mizuno, W.-X. Zhang, Y. Mine, H. Furukawa and S. Kagawa, J. Phys. Chem. 96 (1992) 9360.

[3] K.C.C. Kharas, H.J. Robota and D.J. Liu, Appl. Catal. B 2 (1993) 225.

[4] A. Martinez, S.A. Gomez and G.A. Fuentes, *Catalyst Deactivation* (1997) p. 225.

[5] J.Y. Yan, G.-D. Lei, W.M.H. Sachtler and H.H. Kung, J. Catal. 161 (1996) 43.

[6] T. Tanabe, T. Iijima, A. Koiwai, J. Mizuno, K. Yokota and A. Isogai, Appl. Catal. B 6 (1995) 145.

[7] J.N. Armor and T.S. Farris, Appl. Catal. B 4 (1994) L11.

[8] P. Budi, E. Curry-Hyde and R.F. Howe, Stud. Surf. Sci. Catal. 105 (1997) 1549.

[9] T. Inui, T. Hirabayahi, S. Iwamoto and S. Shimizu, Catal. Lett. 27 (1994) 267.

[10] T. Inui, Stud. Surf. Sci. Catal. 97 (1995) 277.

[11] S. Iwamoto, S. Kon, S. Yoshida and T. Inui, Stud. Surf. Sci. Catal. 105 (1997) 1587.

[12] K. Kagawa, S. Kon, S. Iwamoto and T. Inui, Catal. Lett. 52 (1998) 139.

[13] T. Inui, ACS Symp. Ser. 398 (1989) 752.

[14] T. Inui, S. Iwamoto, S. Kon, T. Sakimon and K. Kagawa, Catal. Today 38 (1997) 169.

[15] B. Kraushaar-Czarnetzki, W.G.M. Hoogervorst, R.R. Andrea, C.A. Emeis and W.H.J. Stork, J. Chem. Soc. Faraday Trans. 87 (1991) 6, 891.

[16] L.E. Iton, I. Choi, J.A. Desjardins and V.A. Maroni, Zeolites 9 (1989) 535.

[17] P. Budi and R.F. Howe, Catal. Today 38 (1997) 175.

[18] M.W. Makinen, L.C. Kuo, M.B. Yim, G.B. Wells, J.M. Fukuyama and J.E. Kim, J. Am. Chem. Soc. 107 (1985) 5245.

[19] E.P. Parry, J. Catal. 2 (1963) 371.

[20] A. Jentys, A. Lugstein and H. Vinek, Zeolites 18 (1997) 391.

[21] Y. Okamoto, T. Adachi, K. Nagata, M. Odawara and T. Imanaka, Appl. Catal. 73 (1991) 249.

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

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

[24] S. Iwamoto, S. Shimizu and T. Inui, Stud. Surf. Sci. Catal. 84C (1994) 1523.

[25] T. Inui, Stud. Surf. Sci. Catal. 105 (1997) 1441.