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NO removal by CH_4 on Co-NaX-CO and Ag-NaX catalysts in a dual-bed system

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Abstract

NO removal using CH_4 as a reductant in a dual-bed system has been investigated with Co-NaX and Ag-NaX catalysts, which were prepared by Co^{2+}-, Ag^{+}-ion exchange into zeolite NaX, respectively, and activation for 5 h at 500 °C. The experimental result has been compared with that of a Co-NaX-CO catalyst, additionally pre-treated under CO flow for the Co-NaX catalyst. The cobalt crystal structure of a Co-NaX-CO catalyst is Co_3O_4, which promotes NO oxidation to NO_2 by excess O_2 at a low temperature (523 K). The mechanical mixture of Co-NaX-CO and Ag-NaX catalysts shows a synergy effect on NO reduction to N_2 by CH_4 in the presence of excess O_2 and H_2O, but the NO reduction decreases quickly as time passes. However, the NO reduction to N_2 in a deNO bed at 523 K and a deNO_2 bed at 423 K, which are relatively lower than the reaction temperatures for common SCR systems, still remained at 67% even in a H_2O 10% gas mixture after 160 min.

Keywords: NO; Zeolite; NaX; Cobalt; Silver; Dual-bed; CH_4

1. Introduction

Hydrocarbon-selective catalytic reduction (HC-SCR) technology has some advantages, such as no NH_3 slip, no potential hazards of NH_3 storage and handling, and low capital investment. And, this process is favored in the presence of excess O_2 [1]. Methane is conventionally regarded as a reducing agent for NO in the presence of O_2.

Transition metal ion-exchanged catalysts have been known to be active for CH_4-SCR [2,3]. Co-zeolite catalyst is suitable for CH_4-SCR in a higher reaction temperature (673–773 K) rather than those of the general SCR processes [1,4], which brings an increase in the LNG consumption of the total SCR process [5].

Several experimental results for the HC-SCR process showed that NO oxidation to NO_2 is the first step of a Co-zeolite catalyst [6], which seems NO_2 plays an important role as an intermediate in this process. Ag-zeolite promotes NO_2 reduction with excellent hydrocarbon efficiency at temperatures as low as 473 K [7,8]. As zeolite NaX has a maximum adsorption capacity at a low concentration of NO_2 [9], it is often selected as a catalyst support. A reduction of NO to N_2 in the presence of excess O_2 and H_2O is not easy at lower temperatures, but the removal of NO and NO_2 from flue gases can be effectively controlled in a dual-bed catalyst system. Thus, a practical alternative to reduce NO emissions, which uses a Co-zeolite as a deNO catalyst at a lower temperature, was investigated in the dual-bed system, consisting of deNO and deNO_2 catalyst beds in a series.

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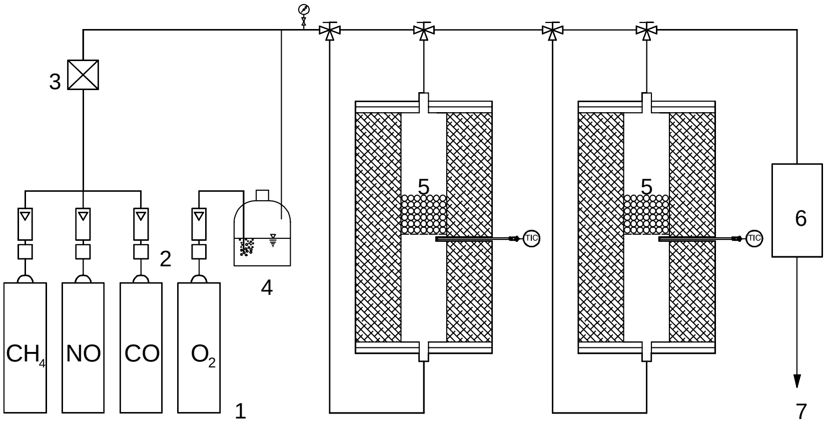

Fig. 1. Schematic diagram of experimental apparatus: (1) gas bomb; (2) mass flow controller; (3) gas mixer; (4) water supplier; (5) catalyst bed; (6) automatic gas analyzer; (7) vent.

2. Experimental

The reactor system used in this experimental is illustrated in Fig. 1. A commercial zeolite NaX (Aldrich, Molecular sieves, 13X, 1.6 mm pellet, Lot. No. 0171 5KR) was used as a catalyst support. Co-NaX and Ag-NaX catalysts were prepared as follows: zeolite NaX was Co^{2+}-ion and Ag^{+}-ion exchanged by 0.25 N $Co(NO_3)_2\cdot 6H_2O$ (Showa, 97%) and $AgNO_3$ (Showa, 99.8%) aqueous solution, respectively, repeated for three times at 296 K. Both ion-exchanged zeolite precursors were calcined at 823 K for 24 h. A Co-NaX-CO catalyst was pre-treated using a Co-NaX catalyst at 773 K for 72 h in a 10–20 ml/min CO flow, and purged by N_2 to remove the CO remaining on the catalyst surface.

The catalytic reaction was carried out for O_2 (99.9%) by changing 0–95 ml/min under 423–723 K, NO 500 ml/min and CH_4 500 ml/min. The space velocity was 9500 h^{-1}, and the gas mixture concentration was adjusted by a mass flow controller (MKS, type 1179). The gas concentrations were analyzed with an automatic flue gas analyzer (TESTO 350) for NO, NO_2 and O_2, and a gas detection pump kit (Gastec, Kitakawa AP-400) for N_2O (0.5–30 ppm) and CH_3NO_2 (5–300 ppm) and the humidity of the flue gas was measured by a hygrometer (TESTO 601).

The contents of Co and Ag within a catalyst were analyzed with an inductively coupled plasma-atomic emission spectrometer (ICP-AES Perkin-Elmer, Optima 4300) for the aqueous solution samples after an ion-exchange. A phase change of a catalyst was analyzed with an X-ray diffractometer (XRD, Philips, X'spert MPD).

3. Results and discussion

3.1. Co-NaX-CO catalyst

The ion exchange amounts were 0.033 meq/g zeolite for Co^{2+}-ion exchanged zeolite and 0.02 meq/g zeolite for Ag^{+}-ion exchanged zeolite. The contents of Co and Ag within the catalysts after calcination were 9.8, 21.0 wt.%, respectively.

The catalytic property of zeolite is closely related to its ability to adsorb a variety of molecular species into the crystal [10]. CO is sensitive to the strong electrostatic fields surrounding transition metal cations in the zeolite structure, interacting specifically with the cationic Lewis acid sites. Therefore, pre-treatment under a CO flow was applied to the Co-NaX catalyst, forming Co oxides (CoO, Co_3O_4, etc.) on the Co-zeolite catalyst. These oxide clusters promote a hydrocarbon combustion and NO_2 formation [11,12].

XRD patterns in Fig. 2 show that Co is not transformed into the Co oxide, Co_3O_4, until the pre-treatment in a CO flow.

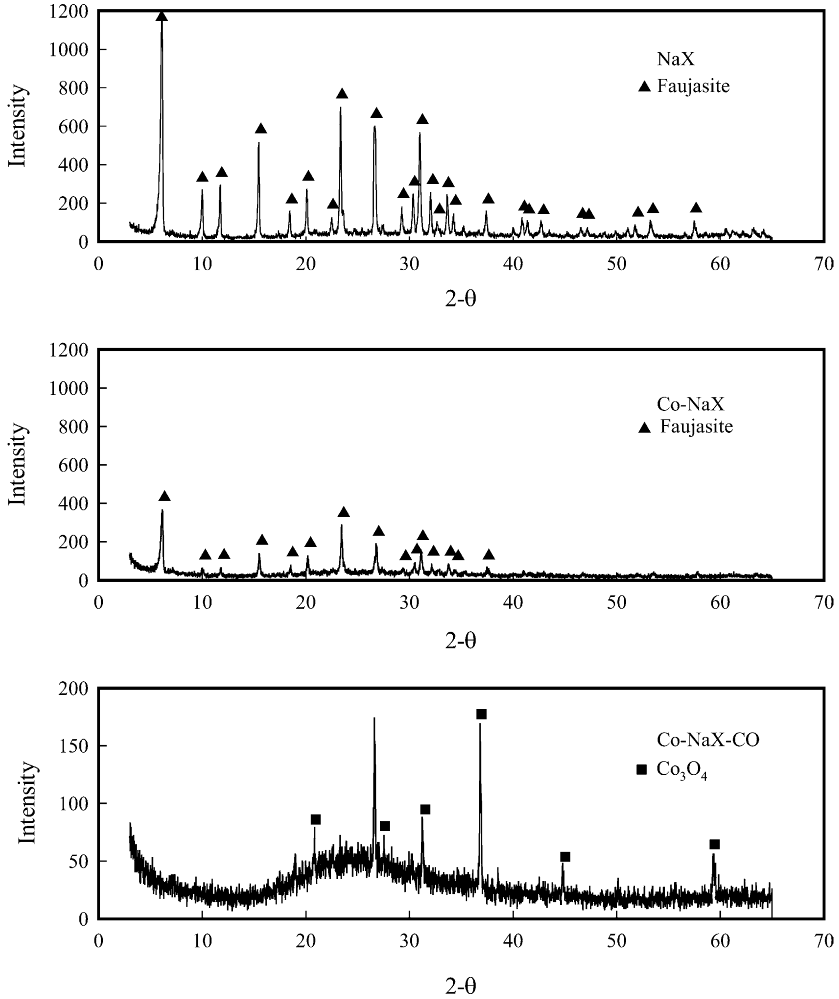

Fig. 2. XRD patterns of NaX zeolite, Co-NaX, and Co-NaX-CO catalysts.

3.2. NO control on Co-NaX-CO catalyst

NO conversions to N_2, NO_2 are defined as lower equations, and N_2O is not considered here because it is not detected by a gas detector.

$$\mathrm{NO\ to\ N_2} = \frac{[\mathrm{NO}_{x,\mathrm{in}} - \mathrm{NO}_{x,\mathrm{out}}]}{\mathrm{NO}_{\mathrm{in}}} 100 \qquad (1)$$

$$\mathrm{NO\ to\ NO_2} = \frac{[\mathrm{NO}_{2,\mathrm{out}} - \mathrm{NO}_{2,\mathrm{in}}]}{\mathrm{NO}_{\mathrm{in}}} 100 \qquad (2)$$

$$\mathrm{NO}_x\ \mathrm{to\ N_2} = \frac{[\mathrm{NO}_{x,\mathrm{in}} - \mathrm{NO}_{x,\mathrm{out}}]}{\mathrm{NO}_{x,\mathrm{in}}} 100 \qquad (3)$$

The effects of reaction temperature on NO_x conversions to N_2, NO_2 on the Co-NaX and Co-NaX-CO catalysts under excess O_2 8.2%, NO 400 ppm, and CH_4 400 ppm are shown in Fig. 3. The NO conversion to NO_2, calculated by using Eq. (2), increases with temperature and reaches a maximum, and then decreases again. An optimum reaction temperature when using the Co-NaX-CO catalyst, obtained at a maximum NO conversion to NO_2 and N_2, is around 523 K, where the NO conversions to NO_2 and N_2 are 52 and 16%, respectively. On the other hand, the NO conversion to NO_2 and N_2 on the Co-NaX catalyst reaches a maximum at 623 K but it does not exceed 20%. This result

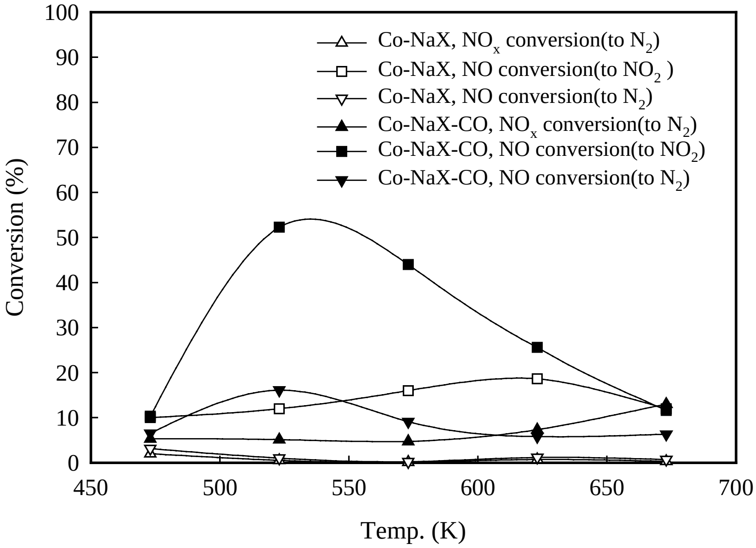

Fig. 3. Effect of reaction temperature on NO conversion to NO_2, N_2 over Co-NaX and Co-NaX-CO catalysts (NO 400 ppm, CH_4 400 ppm, O_2 8.2%, GHSV = 9500 h^{-1}).

means that the NO oxidation to NO_2 is enhanced in excess O_2 and a Co_3O_4 crystal structure.

The reaction of $CH_4/NO/O_2$ on the Co-zeolite catalyst is known to be accomplished by the breaking of the single C–H bond, combination of CH_3 with NO_2, and then the production of CH_3NO_2 [4,13], which is supposed to be a potential intermediate in a CH_4-SCR system. But, CH_3NO_2 is detected very low at 523 K in this study, which indicates that most of the NO oxidizes to NO_2 on the Co-NaX-CO catalyst.

The concentration of O_2 in the reaction gas is an important variable, as oxygen competes with NO for the reductant [14,15]. Fig. 4 shows an effect of O_2

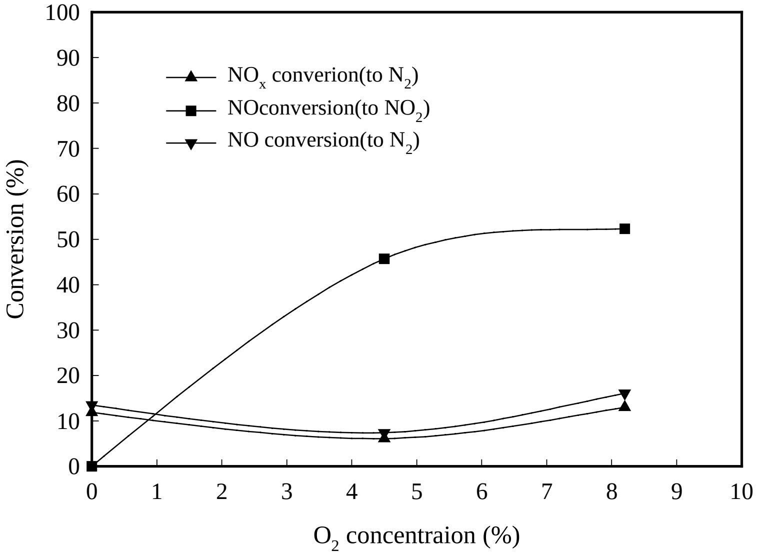

Fig. 4. Effect of O_2 concentration on NO conversion to NO_2, N_2 over Co-NaX-CO catalyst (temp. = 523 K, GHSV = 9500 h^{-1}).

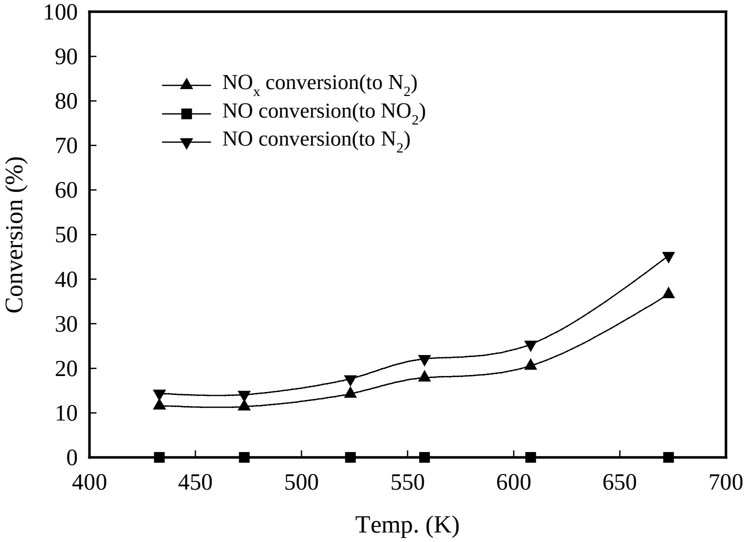

Fig. 5. Effect of temperature on NO conversion to NO_2, N_2 over Ag-NaX catalyst (NO 400 ppm, CH_4 400 ppm, O_2 8.2%, GHSV = 9500 h^{-1}).

concentration on NO conversions to NO_2, N_2 on the Co-NaX-CO catalyst at 523 K. A zero conversion to NO_2 is obtained in the absence of O_2, but an addition of 4.5–8.2% leads to an increase. Since an adsorption of NO_2 on the Co^{2+} site is a necessary step [4], O_2 is essential for NO conversion on the Co-zeolite catalyst. Thus, on the Co-NaX-CO catalyst at 523 K, the NO conversion to NO_2 is supposed to be carried out via O_2 adsorption, whereas, the conversion to N_2 is done via the intermediate in the presence of 4.5–8.2% excess O_2.

3.3. NO control using the Ag-NaX catalyst

CH_4-SCR reaction on the Ag-NaX catalyst at different temperatures (423–673 K) shows a typical result that NO conversion depends on temperature, as shown in Fig. 5. The Ag-zeolite catalyst is generally not highly active in HC-SCR, that is, the maximum NO conversion is mostly below 30% [16]. The NO reduction to N_2 increases with reaction temperature but NO oxidation to NO_2 does not occur in this study, which can be explained by the NO removal reaction below [17].

$$2NO + CH_4 + O_2 \rightarrow N_2 + CO_2 + 2H_2O \tag{4}$$

3.4. NO control using a dual-bed system (Co-NaX-CO and Ag-NaX)

In order to improve the NO removal process, a combined system of two catalytic beds in a series has been adapted. NO is to be oxidized to NO_2 by methane on the Co-NaX-CO catalyst (deNO) in the first bed, and NO_2 is to be reduced to N_2 by methane on the Ag-NaX catalyst (deNO_2) in the second one. If the NO conversion is satisfied when applied to the two catalysts in a single-bed reactor, this single-bed system is economically more favored than a dual-bed system.

The performance of a mechanical mixture of 70 wt.% Co-NaX-CO and 30 wt.% Ag-NaX at 523 K for NO/CH_4/O_2 gas mixture is shown in Fig. 6. Mechanical mixing of the NO oxidation catalyst and NO_2 reduction catalyst generally gives a synergy effect [18]. In this study, the mechanical mixture catalyst in a single-bed exhibits the synergy effect on NO control even in the presence of excess O_2 and H_2O.

NO conversion to N_2 shows so highly that mostly all of the NO reduces to N_2 in the first 5 min, which must be an obvious example of the synergy effect. However, NO reduction to N_2 decreases down to 54% in the next 7 min, and continues to decrease to about 12% for the next 140 min. At the same time, the NO

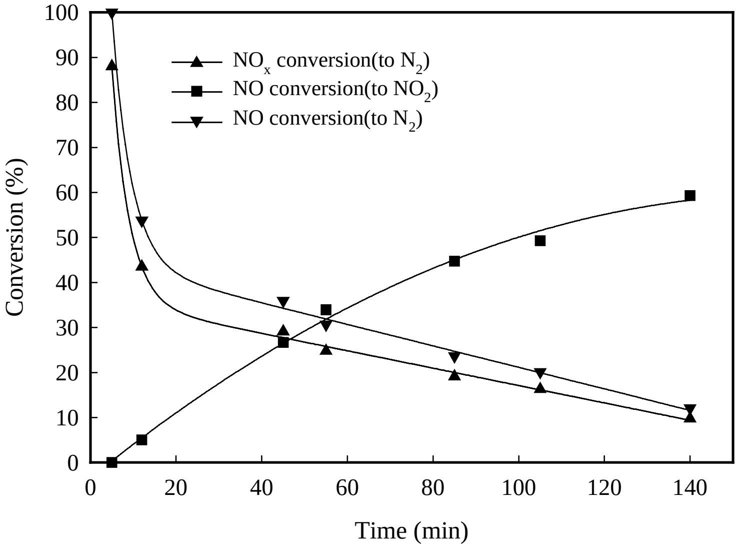

Fig. 6. Effect of reaction time on NO conversion to NO_2, N_2 over mechanical mixture of Co-NaX-CO catalyst (70%) and Ag-NaX catalyst (30%) (temp. = 523 K, NO 400 ppm, CH_4 400 ppm, O_2 8.2%, GHSV = 9500 h^{-1}).

oxidation to NO_2 goes on increasing, which seems to be caused by an insufficiency of the Ag-NaX catalyst.

Generally, NO_2 has been proposed to be an important intermediate in the reaction scheme of SCR of NO_x to N_2 [3]. According to this mechanism, for the reaction of the selective reduction of NO by CH_4, there exist three competing reactions as follows:

$$2NO + O_2 \leftrightarrow 2NO_2 \qquad (5)$$

$$NO_2 + CH_4 \leftrightarrow N_2 + CO_2 + 2H_2O \qquad (6)$$

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \qquad (7)$$

In order to promote the NO conversion to N_2, reaction (7) must be inhibited as much as possible. As seen in Fig. 6, reaction (5) gradually becomes the principal as time passes, and the NO conversion to NO_2 reaches 60% after 140 min.

Therefore, an application of a dual-bed system with mechanical mixing is inadequate for NO removal because the NO_2 reduction to N_2 on the Ag-NaX catalyst is too low. Though Ag-NaX catalyst does not promote the NO oxidation to NO_2 for 423–723 K, as shown in Fig. 5, the reaction temperature that enables it to reduce NO_2 to N_2 is indistinct. Another experiment to change the reaction temperature of the deNO$_2$ bed with the Ag-NaX catalyst, as shown in Fig. 7, shows that the temperature range must be maintained between 423 and 473 K to reduce NO_2 to N_2. The NO conversion, via NO_2, to N_2 is about 70% at this temperature range but NO_2 is not detected. The NO reduction to N_2, however, decreases rapidly below 4% as the reaction temperature increases above 473 K, while the NO oxidation to NO_2 increases very quickly. At 573 K, the NO reduction to N_2 does not occur, but the NO oxidation to NO_2 reaches about 65%, which is similar to that of the other study [7]. Consequently, the operation temperature of the deNO$_2$ bed must be maintained within 423–473 K.

The actual operation temperature of the deNO$_2$ bed in this study was set at 423 K, because the reaction temperature is low, as the energy consumption rate is less. At this temperature, a stability of a deNO and deNO$_2$ catalysts in a dual-bed system was tested in a flow of a gas mixture composed of NO 396 ppm, CH_4 396 ppm, O_2 8.2%, and H_2O 10%, which is shown in Fig. 8. The NO conversions to NO_2, N_2 are 0, 100%, respectively, in the initial stages, which are supposed to be caused by a synergy effect. After 15 min, the NO reduction to N_2 decreases down to 85%, which can be explained that NO converts to N_2 through an intermediate NO_2 as seen in reaction (6). The NO reduction to N_2 in the deNO bed at 523 K and the deNO$_2$ bed

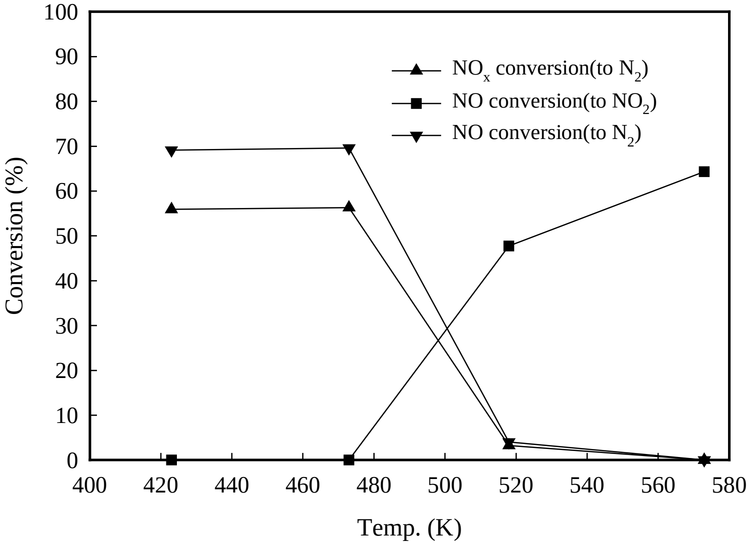

Fig. 7. Effect of reaction temperature of deNO$_2$ bed (Ag-NaX) on NO conversion to NO$_2$, N$_2$ (NO 400 ppm, CH$_4$ 400 ppm, O$_2$ 8.2%, GHSV = 9500 h^{-1}).

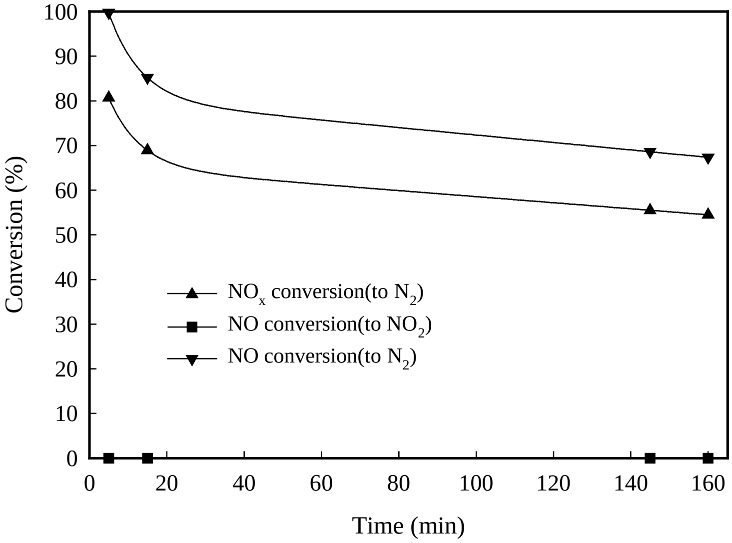

Fig. 8. Stability of deNO (523 K)-deNO$_2$ (423 K) beds in a dual-bed system (NO 396 ppm, CH$_4$ 396 ppm, O$_2$ 8.2%, H$_2$O 10%, GHSV = 9500 h^{-1}).

at 423 K, which are relatively lower than the reaction temperatures for common the SCR systems, still remained at 67% even in a H$_2$O 10% gas mixture after 160 min.

4. Conclusions

For the catalytic reduction of NO by CH$_4$ in the presence of O$_2$ and H$_2$O, a dual-bed catalyst

Table 1
Inlet gas compositions

Conditions	NO (ppm)	NO_2 (ppm)	CH_4 (ppm)	O_2 (%)	H_2O (%)
1	496	–	496	–	–
2	420	75	420	4.5	–
3	400	95	400	8.2	–
4	396	100	396	8.2	10.0

system, should be composed of a deNO bed with a Co-NaX-CO catalyst and a $deNO_2$ bed with a Ag-NaX catalyst, which is active at lower temperatures (523 K for deNO and 423 K for $deNO_2$) unlike those of the common SCR system. The cobalt crystal structure on a Co-NaX-CO catalyst is changed to Co_3O_4, which may promote NO oxidation to NO_2 by excess O_2 at a low temperature (523 K). The mechanical mixture of the Co-NaX-CO and Ag-NaX catalysts shows a synergy effect on NO reduction to N_2 by CH_4 in the presence of excess O_2 and H_2O, but this NO reduction decreases quickly as time passes. However, the NO reduction to N_2 in a deNO bed at 523 K and a $deNO_2$ bed at 423 K, which are relatively lower than the reaction temperatures for the common SCR systems, still remained at 67% even in a H_2O 10% gas mixture after 160 min (Table 1).

Acknowledgements

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References

[1] J.N. Armor, Catal. Today 26 (1995) 147.
[2] X. Zhang, A.B. Walters, M.A. Vannice, Catal. Today 27 (1996) 41.
[3] L. Ren, T. Zhang, D. Liang, C. Xu, J. Tang, L. Lin, Appl. Catal. B 35 (2002) 317.
[4] F. Seyedeyn-Azad, D.K. Zhang, Catal. Today 68 (2001) 161.
[5] M. Braford, R. Grover, in: Proceedings of the IT3'01 Conference, Philadelphia, PA, 14–18 May 2001.
[6] Y. Li, T.L. Slager, J. Armor, J. Catal. 150 (1994) 388.
[7] P.A. Jacobs, I. Lievens, J.A. Martnens, European Patent Application 697 240, assigned to Regie Nationale des Usines Renault, 21 February 1996.
[8] J.A. Martens, A. Cauvel, A. Francis, C. Hermans, F. Jayat, M. Remy, M. Keung, J. Lievens, P.A. Jacobs, Angew Chem. Int. Ed. Engl. 37 (1998) 1901.
[9] Z.M. Wang, T. Arai, M. Kumagai, Energy Fuels 12 (1998) 1055.
[10] V.M. Rakic, R.M. Hercigonja, V.T. Dondur, Microporous Mesoporous Mater. 27 (1999) 27.
[11] S.E. Maisuls, K. Seshan, S. Feast, J.A. Lercher, Appl. Catal. B 29 (2001) 69.
[12] H. Ohtsuka, T. Tabata, O. Okada, L.M.F. Sabatino, G. Bellussi, Catal. Today 42 (1998) 45.
[13] N.W. Cant, I.O.Y. Liu, Catal. Today 63 (2000) 133.
[14] C.S. Shin, T.H. Lee, Hwahak Gonghak 4 (27) (1989) 588.
[15] M.H. Kim, I.S. Nam, Y.G. Kim, J.K. Lee, D.K. Park, Hwahak Gonghak 3 (32) (1994) 402.
[16] Y. Traa, B. Burger, J. Weitkamp, Microporous Mesoporous Mater. 30 (1999) 3.
[17] Y. Li, J.N. Armor, J. Catal. 150 (1994) 376.
[18] J.A. Martens, A. Cauvel, F. Jayat, E. Jobson, Appl. Catal. B 29 (2001) 299.