Selective reduction of nitric oxide by methane on cobalt-ion-exchanged synthetic clinoptilolite zeolite in oxygen-rich atmosphere

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Selective reduction of NO by CH_4 in the presence of excess O_2 has been studied on cobalt-ion-exchanged synthetic clinoptilolite (Co-CLI) zeolite. The catalytic results are compared with those obtained from Co-ZSM-5 and Co-FER, the two most widely studied catalysts for this reaction. At $T \geqslant 500\,^{\circ}C$, Co-CLI is much more active for NO reduction than Co-ZSM-5, but it is less active than Co-FER. However, it is found that the selectivity for CH_4 toward reacting with NO at high temperatures ($T \geqslant 450\,^{\circ}C$) is higher on Co-CLI than on Co-ZSM-5 or Co-FER. On the basic of the overall catalytic results, the importance of zeolite pore size as a structural parameter influencing the activity of intrazeolitic Co^{2+} ions for NO reduction by CH_4 is discussed.

Keywords: synthetic clinoptilolite, cobalt, NO reduction, CH_4, zeolite pore structure

1. Introduction

Clinoptilolite is the most abundant of natural zeolites and is classified as the silica-rich member (Si/Al > 4) of the heulandite (HEU) group of zeolites [1,2]. The framework topology of HEU-type zeolites is characterized by a two-dimensional pore system consisting of 8-ring channels (2.6×4.7 Å) that intersect two parallel 10-ring channels (3.0×7.6 Å) and 8-ring channels (3.3×4.6 Å) [3].

Natural clinoptilolite has found applications in ion exchange, gas separation, and radioactive waste removal processes [4–8]. However, the use of this zeolite as a catalyst is hampered due to the difficulty in completely eliminating the metal impurities, most notably iron, that are commonly found in the natural sample as oxides and hydroxides both in the zeolite framework. Consequently, many attempts have been made to synthesize an impurity-free clinoptilolite using an alkali-metal aluminosilicate gel as a starting phase [9–15]. The knowledge accumulated so far reveals that pure clinoptilolite can be prepared under typical hydrothermal conditions, although the crystallization conditions and the composition of reaction mixtures leading to a successful clinoptilolite formation are restricted within narrow limits. However, little attention has thus far focused on the catalytic application for the synthetic clinoptilolite zeolite [16].

Abatement of toxic nitrogen oxides (NO_x) produced on a massive scale during the combustion of fossil fuels at high temperatures is one of the most urgent and demanding challenges in environmental catalysis [17,18]. In particular, the emission control of nitrogen monoxide (NO) is the major target to be accomplished. The selective catalytic reduction (SCR) by NH_3 is the current, best available technology for removing NO from the oxygen-rich exhausts of stationary combustion sources. However, the use of NH_3 as a reductant is not suitable for applications in mobile combustion sources. This has triggered the continual search for catalysts which could reduce effectively NO in the presence of hydrocarbons. The discovery by Held et al. [19,20] and Iwamoto et al. [21] that copper-ion-exchanged ZSM-5 (Cu-ZSM-5) zeolite is much more effective than earlier catalysts for NO reduction in an oxidizing atmosphere with many hydrocarbons, except methane, offered a major breakthrough to researches in this field, although there is a serious drawback in its use as a full-scale NO reduction catalyst due to the poor stability under thermal and hydrothermal conditions. On the other hand, Li and Armor have reported that cobalt-ion-exchanged ZSM-5 (Co-ZSM-5) catalyst is highly active for the selective reduction of NO using CH_4, especially in the presence of excess O_2 [22,23]. They have found that Co^{2+}-exchanged ferrierite (Co-FER) is a more active catalyst for this reaction; the activity for the NO reduction on Co-FER is twice that for Co-ZSM-5 at 550 °C [24].

It is well established that the catalytic activities of metal-ion-exchanged zeolites for the reduction of NO by CH_4 in excess O_2 are highly dependent not only on the type of exchanged metal ions, but also on the framework topology of zeolites used as supports [20–24]. However, the structural

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requirement of zeolite supports for an effective catalyst is not well understood. Natural clinoptilolite is reported to exhibit an excellent selectivity for Co^{2+} ions, as well as other metal cations such as Cs^{+} and Sr^{2+} ions [7,8]. As stated above, in addition, this zeolite contains intersecting 8- and 10-ring channels like FER zeolite. Therefore, it is of fundamental interest to investigate the catalytic behavior of Co^{2+}-exchanged clinoptilolite for the NO SCR by CH_4 in excess O_2 in order to better understand the effect of zeolite pore structure on the NO reduction activity of intrazeolitic Co^{2+} ions. Here we report on the reactivity of Co^{2+}-exchanged synthetic clinoptilolite and compare the results to those obtained from Co-FER and Co-ZSM-5 catalysts that are among the most active catalysts for this reaction.

2. Experimental

A clinoptilolite zeolite with Si/Al = 5.8 was synthesized using a seeding technique following the procedure described previously [16]. Here we refer to this synthetic clinoptilolite as CLI. A Co^{2+}-exchanged CLI (Co-CLI) zeolite with Co/Al = 0.36 was prepared by a two-step ion-exchanged process. First, the CLI sample synthesized as the mixed Na, K cation form, i.e., NaK-CLI, was converted to its ammonium form (NH_4-CLI) by refluxing twice in 1.0 M NH_4NO_3 solutions for 6 h. Then, the NH_4-CLI sample was exchanged with 0.02 M $Co(CH_3CO_2)_2$ solutions at 80 °C for 24 h. Finally, the zeolite was calcined in air at 500 °C for 12 h. For comparison, Co-FER (Si/Al = 9.0 and Co/Al = 0.36) and Co-ZSM-5 (Si/Al = 13.5 and Co/Al = 0.48) catalysts were prepared with procedures similar to the Co-CLI preparation. NaK-FER and NH_4-ZSM-5 zeolites, used as starting materials for ion exchange, were purchased from Tosoh and ALSI-PENTA Zeolithe GmbH, respectively.

The powder X-ray diffraction patterns of the zeolite samples were recorded on a Rigaku D/Max-IIIA diffractometer (Kα radiation). Chemical analysis was performed using a Jarrell–Ash Polyscan 61E inductively coupled plasma spectrometer in conjunction with a Perkin–Elmer 5000 atomic absorption spectrophotometer. The chemical compositions of zeolites used here are given in table 1. The nitrogen BET surface areas were measured on a Micromeritics ASAP 2000 analyzer. The acidic properties of the zeolites were determined by temperature-programmed desorption (TPD) of ammonia using a TPD apparatus described elsewhere [16].

Table 1
Chemical compositions and BET surface areas of zeolites used in this study.

Material	Anhydrous unit cell composition	Si/Al	Co/Al	BET surface area[a] ($m^2\ g^{-1}$)
H-ZSM-5	$H_{6.6}Al_{6.6}Si_{89.4}O_{192}$	13.5		429
H-FER	$H_{3.6}Al_{3.6}Si_{32.4}O_{72}$	9.0		381
H-CLI	$H_{5.3}Al_{5.3}Si_{30.7}O_{72}$	5.8		386
Co-ZSM-5	$Co_{3.2}H_{0.2}Al_{6.6}Si_{89.4}O_{192}$	13.5	0.48	376
Co-FER	$Co_{1.3}H_{1.0}Al_{3.6}Si_{32.4}O_{72}$	9.0	0.36	347
Co-CLI	$Co_{1.9}H_{1.5}Al_{5.3}Si_{30.7}O_{72}$	5.8	0.36	114

[a] BET surface areas calculated from nitrogen adsorption data.

The catalytic activities were measured using a conventional continuous flow microreactor loaded with 0.2–0.5 g of catalyst at 400–650 °C and atmospheric total pressure. The catalyst was activated under flowing He (100 $cm^3\ min^{-1}$) at 500 °C for 2 h and kept at the desired temperature before starting a reaction run. Then, a reactant stream consisting of 1640 ppm NO, 1000 ppm CH_4, and 2.5% O_2 with He as a balancing gas was passed through the catalyst at a total flow rate of 200 $cm^3\ min^{-1}$. The typical gas hourly space velocity (GHSV) was 30 000 or 12 000 h^{-1} based on the apparent bulk density of the zeolite catalysts, ca. 0.5 $g\ cm^{-3}$. The reaction products were analyzed on-line in a Gow–Mac gas chromatograph equipped with a thermal conductivity detector, and a Molecular Sieve 5A column was used in order to separate N_2, O_2, and CH_4. The NO conversion was calculated based on the N_2 formation, and the CH_4 conversion was obtained by following changes in the CH_4 peak area. CO was not observed as a product of CH_4 oxidation, which was thus 100% selective to CO_2. A Jung CX-8AN NO_x analyzer and a Siemens Ultramat 21/CO_2 gas analyzer were also used to check the nitrogen and carbon mass balances, respectively. Selectivity of CH_4, defined as the molar ratio of the CH_4 reacted with NO to the total CH_4 totally consumed, was calculated from the following equation:

$$\text{selectivity} = \frac{0.5[\mathrm{NO}]_0 C_{\mathrm{NO}}}{[\mathrm{CH_4}]_0 C_{\mathrm{CH_4}}} \times 100\%, \tag{1}$$

where $[NO]_0$ is the inlet concentration of NO, C_{NO} is the conversion of NO, and $[CH_4]_0$ and C_{CH_4} are the inlet concentration and conversion of CH_4, respectively. The value, 0.5, is the stoichiometric ratio of NO and CH_4 based on the NO reduction reaction in the presence of CH_4 and O_2, that is, $2NO + CH_4 + O_2 \rightarrow N_2 + CO_2 + 2H_2O$.

3. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of different cation forms of CLI zeolite prepared in this study. The XRD pattern of as-synthesized NaK-CLI zeolite in figure 1(a) is in good agreement with that reported in the literature [25]. No reflections other than those from a zeolite with the HEU structure are observed. As seen in parts (b)–(e) of figure 1, in addition, all the characteristic X-ray peaks of the parent NaK-CLI zeolite remain intact during the NH_4^+ or Co^{2+} ion exchange, calcination, and NO reduction. For example, the XRD pattern of H-CLI zeolite obtained by heating NH_4-CLI at 500 °C is essentially identical with that of NaK-CLI zeolite, except that the relative peak intensities and positions are somewhat different. The same result was also obtained from the Co-CLI zeolites before and after NO reduction at temperatures up to 650 °C.

No detectable peaks from metallic or oxide form of cobalt are found in their XRD patterns. Therefore, it is clear that the Co-CLI sample prepared here has high thermal stability.

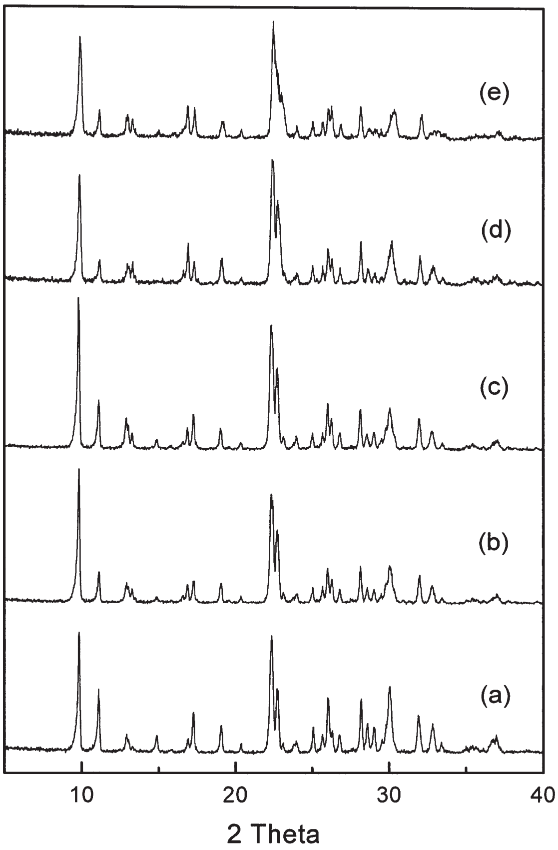

Figure 1. Powder X-ray diffraction patterns of different cation forms of clinoptilolite zeolite synthesized in this study: (a) NaK-CLI, (b) NH_4-CLI, (c) H-CLI, and Co-CLI zeolites (d) before and (e) after NO selective reduction.

Figure 2 shows the NH_3 TPD profiles obtained from Co-CLI, Co-ZSM-5, and Co-FER zeolites together with those from the proton forms of the corresponding materials. These TPD results reveal that Co^{2+} ion exchange in zeolites studied here is accompanied by dramatic alteration of their acidic properties. As seen in figure 2(a), for example, H-CLI exhibits two desorption peaks at 240–260 and 560–580 °C. In the TPD profile of Co-CLI, however, the desorption peak at 560–580 °C is hardly visible. Also, a new one appears at 660–680 °C. The NH_3 TPD measurements of three Co-CLI zeolites with different exchange levels (Co/Al = 0.10–0.36) have demonstrated that the intensity of the desorption peak at 660–680 °C increases with Co content. Therefore, it is most likely that this high-temperature peak can be assigned to NH_3 desorption from the Co^{2+} ions in Co-CLI. This is not unexpected, because the intrazeolitic Co^{2+} ion can serve as an excellent Lewis acid center [26]. A similar type of acid sites, but of slightly lower strength than in Co-CLI, is also present in Co-ZSM-5 and Co-FER. As shown in parts (b) and (c) of figure 2, Co-ZSM-5 and Co-FER give a rather large desorption peak at 640–660 °C that is completely missing in the profiles of both H-ZSM-5 and H-FER. Unlike H-ZSM-5, in particular, Co-ZSM-5 exhibits an NH_3 desorption shoulder around 370 °C in the temperature region 250–500 °C, which is consistent with the recent work of Li and Armor [27]. This suggests that another type of Lewis acid sites that possesses an intermediate acid strength exists in Co-ZSM-5. The chemical composition data in table 1 reveal that none of the zeolites studied here was fully exchanged with Co^{2+} ions and, thus, they are not free of Brønsted acid sites. As a result, no conclusion on the nature of their acid sites (Brønsted acidity vs. Lewis acidity) can be drawn from the NH_3 TPD measurements alone. However, the NH_3 TPD results in figure 2 clearly show that the strength and distri-

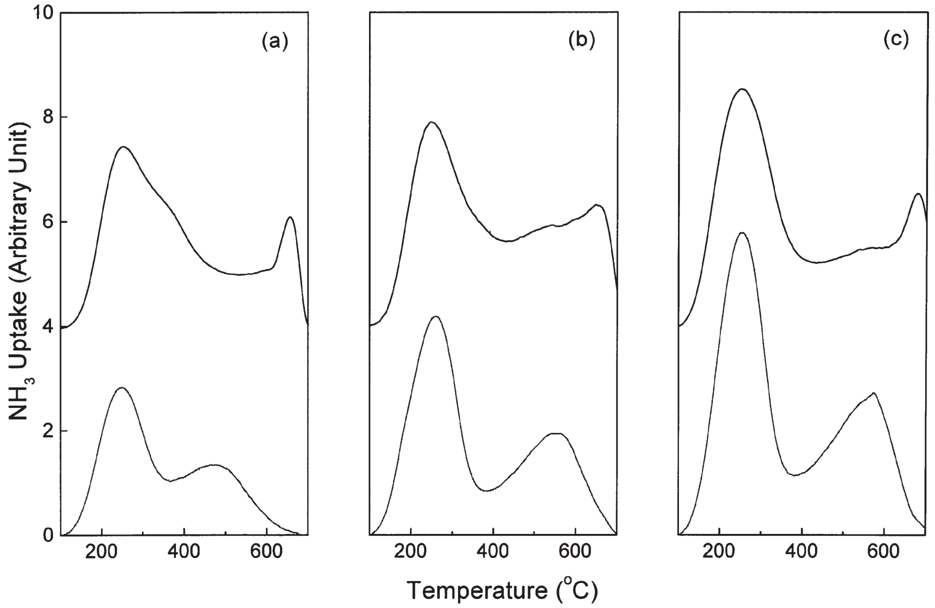

Figure 2. NH_3 TPD profiles from proton (bottom) and cobalt (top) forms of (a) ZSM-5, (b) FER, and (c) CLI zeolites. The heating rate is 10 °C min^{-1}.

bution of the Lewis acid sites, at least generated by Co^{2+} ion exchange, are not the same for the three zeolites studied in this work. This can be attributed to differences in the local environment of intrazeolitic Co^{2+} ions, which originated from the unique pore structure of each zeolite.

Figure 3 compares the NO conversions on Co-ZSM-5, Co-FER, and Co-CLI zeolites measured as a function of reaction temperature at 30 000 h^{-1} GHSV, 1640 ppm NO, 1000 ppm CH_4, and 2.5% O_2 in the feed. The Co-ZSM-5 zeolite with two intersecting 10-ring channels exhibits a maximum NO conversion of 25% at 450 °C, and the conversion curve bends over at $T > 450\,^\circ C$. Such a bending over of NO conversion is also observed for the Co-FER and Co-CLI zeolites with intersecting 8- and 10-ring channels. As shown in figure 3, for example, the maximum NO conversion on Co-FER is 48% at 500 °C, a 50 °C shift upward. Thus, Co-FER yields about twice the NO conversion compared to Co-ZSM-5 at $T \geqslant 500\,^\circ C$. This result is consistent with that reported in the literature [22]. Like Co-FER, Co-CLI has a lower activity compared to Co-ZSM-5 at low temperatures (400–450 °C), but it becomes much more active at $T \geqslant 500\,^\circ C$. For example, Co-CLI has a NO conversion of 36% at 550 °C, a factor of about two higher than Co-ZSM-5 at the same temperature. This clearly shows that Co-CLI is an effective catalyst for the reduction of NO by CH_4 in excess O_2, especially at high temperatures. Compared to Co-FER, on the other hand, Co-CLI has a lower NO conversion in the temperature region studied here. However, the difference in NO conversion between Co-FER and Co-CLI becomes smaller at $T > 500\,^\circ C$. Thus, these two catalysts give comparable NO reduction activities at 600–650 °C.

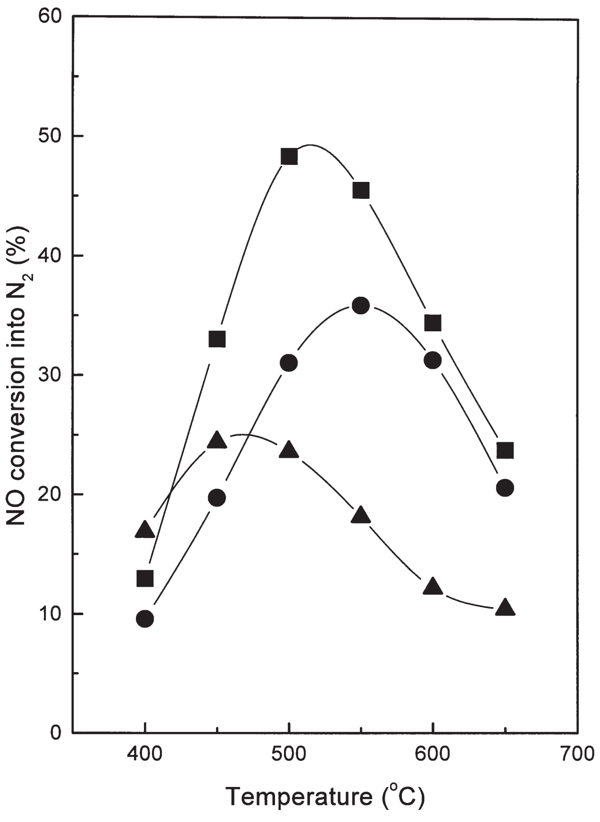

Figure 3. Comparison of NO reduction activities of Co-ZSM-5 (▲), Co-FER (■), and Co-CLI (●) catalysts as a function of temperature. The reactions were run with a feed containing 1640 ppm NO, 1000 ppm CH_4, and 2.5% O_2 at a GHSV of 30 000 h^{-1}.

The zeolite framework normally functions as a huge ligand to coordinate and stabilize its metal cations. Consequently, the nature and extent of interactions between the cations and zeolite framework may depend primarily on the size and shape of the pores where the metal cations are located. Li and Armor have explained the excellent NO conversion of Co-FER at $T > 450\,^\circ C$ by suggesting that the presence of 8-ring channels in FER zeolite leads to a high selectivity for CH_4 toward reacting with NO in excess O_2 [28]. They speculate that the Co^{2+} ion sites in 8-ring channels are thermodynamically more stable with higher coordinations compared to those in 10-ring channels and are more selective in the use of CH_4 for NO reduction due to the smaller pore size. Thus, if this speculation is correct, Co-CLI should have a higher CH_4 selectivity for NO reduction compared to Co-ZSM-5, because of the presence of two different types of 8-ring channels in CLI zeolite. The CH_4 conversions and NO conversions on Co-ZSM-5, Co-FER, and Co-CLI zeolites at different temperatures are given in table 2. These data reveal that CH_4 is completely consumed on Co-ZSM-5 and Co-FER at 550 and 600 °C, respectively. However, Co-CLI was found to exhibit a much lower CH_4 conversion at a higher temperature, e.g., 73% at 650 °C. Apparently, the lower CH_4 conversion on Co-CLI compared to the other two catalysts leads to a much higher CH_4 selectivity. As seen in figure 4, therefore, the selectivity for CH_4 toward reacting with NO is much higher on Co-CLI than on Co-ZSM-5 at any temperature. In addition, it should be noted from figure 4 that the CH_4 selectivity of Co-CLI is higher than that of Co-FER at $T \geqslant 450\,^\circ C$. These results appear to support the point of view that the

Table 2
NO and CH_4 conversions on Co^{2+}-exchanged zeolite catalysts.[a]

	NO conversion (%)						CH_4 conversion (%)					
	400 °C	450 °C	500 °C	550 °C	600 °C	650 °C	400 °C	450 °C	500 °C	550 °C	600 °C	650 °C
Co-ZSM-5	17	25	24	18	12	10	29	55	89	100	100	100
Co-FER	13	33	48	46	34	24	13	41	77	93	100	100
Co-CLI	10	20	31	36	31	21	13	23	39	54	64	73

[a] The reactions were run with a feed consisting of 1640 ppm NO, 1000 ppm CH_4, and 2.5% O_2 at a GHSV of 30 000 h^{-1}.

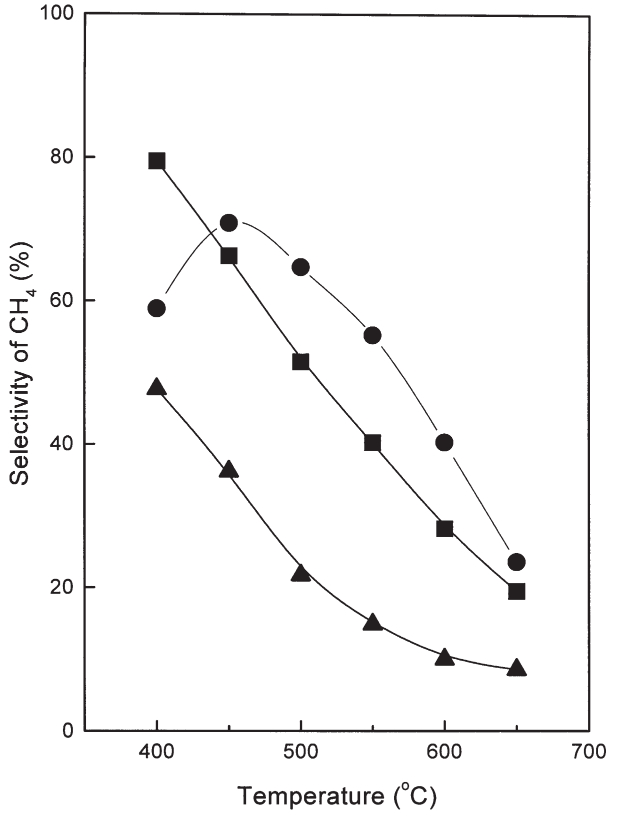

Figure 4. Selectivities of CH_4 over Co-ZSM-5 (▲), Co-FER (■), and Co-CLI (●) catalysts as a function of temperature. The reaction conditions are the same as those in figure 3.

presence of 8-ring channels in zeolite hosts for Co^{2+} ions may play an important role in achieving high activity for NO reduction by CH_4.

There is a general acceptance that the isolated Co^{2+} ions are the active sites for the NO reduction on Co^{2+}-exchanged zeolite catalysts, although not all the cations have the same NO reduction activity or selectivity [23,24,29]. In fact, H-CLI zeolite itself showed no appreciable activity under the reaction conditions employed here. On the other hand, the transition metal cations such as Co^{2+} or Cu^{2+} ions exchanged into zeolites are known to preferentially migrate to the internal sites of zeolites during the thermal treatment step at elevated temperatures that is essential for further ion exchange and/or for catalyst activation [30]. As stated earlier, the CLI zeolite consists of two main channels in the [001] direction, one formed by a 10-ring (3.0 × 7.6 Å) and the other by an 8-ring (3.3 × 4.6 Å). This zeolite also contains another type of 8-ring channels (2.6 × 4.7 Å) in the [100] direction. Therefore, it is most likely that the number of Co^{2+} ions in the 8-ring channels of our Co-CLI may be larger that that of divalent cations in the 10-ring channels of the same catalyst, because all zeolite catalysts of this study were pretreated at 500 °C prior to its use for NO reduction by CH_4. Notice that the effective diameter of Co^{2+} ions lies in the range 1.4–2.1 Å, depending on their coordination number and spin state [31]. This implies that NO reduction with CH_4 cannot occur inside the 8-ring channels of Co-CLI due to steric effects caused by blocking actions of Co^{2+} ions, as well as to the kinetic diameter (3.8 Å) of CH_4 much larger than the effective size of metal-ion-containing 8-ring channels of CLI zeolite. We suspect that the same situation should be also observed for the 8-ring channels in FER zeolite because of their small size (3.5 × 4.8 Å). If the Co^{2+} ions are positioned within the pore mouth of 8-ring channels perpendicular to 10-ring channels in CLI zeolite, in contrast, they could serve as catalytically active sites for the NO reduction by CH_4 without causing a serious diffusional problem. If such is the case, the pore size of the main channels in zeolite supports for Co^{2+} ions must exert an important effect on the selective use of CH_4 for NO reduction. The 10-ring channels (3.0 × 7.6 Å) in CLI zeolite are much more elliptical than those (4.2 × 5.4 Å) in FER zeolite and are smaller than either straight 10-ring channels (5.3 × 5.6 Å) or sinusoidal 10-ring channels (5.1 × 5.5 Å) in ZSM-5. In addition, the larger zeolite channels tend to be more active for CH_4 combustion at higher temperatures. These arguments taken in total lead us to believe that differences in the pore size of the 10-ring channels in zeolite catalysts studied here may be the main origin of the fact that the selectivity of CH_4 for NO reduction in excess O_2 is higher in the order Co-ZSM-5 < Co-FER < Co-CLI, as illustrated in figure 4. In addition, it should be noted that the temperature for maximum NO conversion on these catalysts increases in the same order (see figure 3). This can be rationalized by considering that, among the three zeolite catalysts, Co-CLI may have the highest spatial constraints suppressing the free diffusion of CH_4 with a kinetic diameter of 3.8 Å for NO reduction due to the small size of its 10-ring channels, which can be reduced by elevating reaction temperature.

Figure 5 shows the dependence of NO and CH_4 conversions on the inlet CH_4 concentration over Co-CLI at 550 °C. Addition of 600 ppm CH_4 in a feed containing only NO (1640 ppm) and O_2 (2.5%) greatly enhances the NO conversion from nearly zero to 40%. Upon further increasing CH_4 level, the NO conversion continues to increase linearly up to 67%. On the other hand, the CH_4 conversion decreases with increasing CH_4 concentration, but it is still high, e.g., 55% for 4000 ppm CH_4, giving the CH_4 selectivity of 23% for NO reduction. This again shows that the CLI environment is very selective in the use of CH_4 for NO reduction. To investigate whether O_2 is essential for Co-CLI to perform the reaction with CH_4, the dependence of NO conversions on the inlet O_2 concentration has also been tested on this catalyst at 550 °C and is given in figure 6. Upon increasing O_2 level up to 0.5%, the NO conversion increases very sharply, reaching a maximum value of 51%. The increase of NO conversion with O_2 added has also been observed during the reaction with CH_4 on other Co^{2+}-exchanged zeolites such as Co-ZSM-5 and Co-FER [23,24]. On the other hand, the activity of Co-CLI decreases slightly in the O_2 concentration range 0.5–2.5%. However, it remains almost unchanged at O_2 levels up to

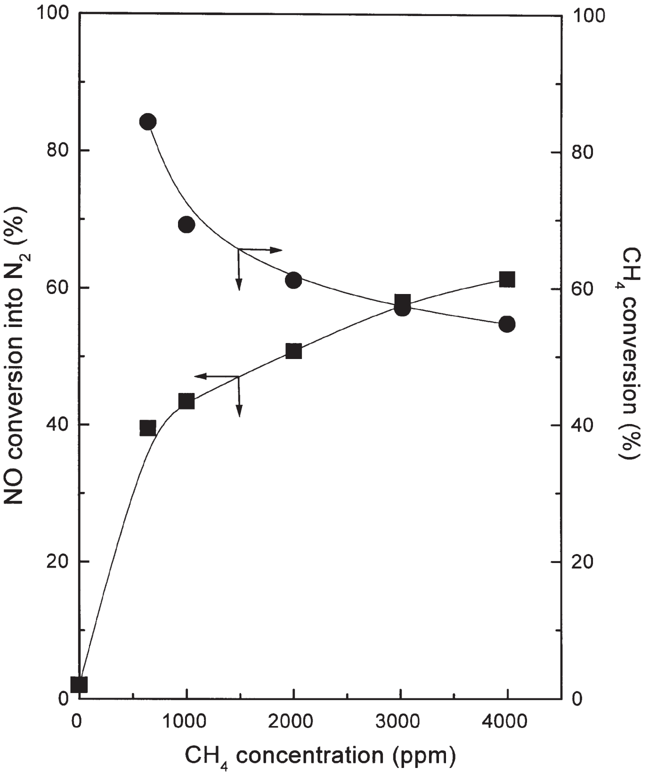

Figure 5. Conversions of NO and CH_4 as a function of inlet CH_4 level on Co-CLI at 550 °C. The reaction was run with a feed consisting of 1640 ppm NO and 2.5% O_2 at a GHSV of 12 000 h^{-1}.

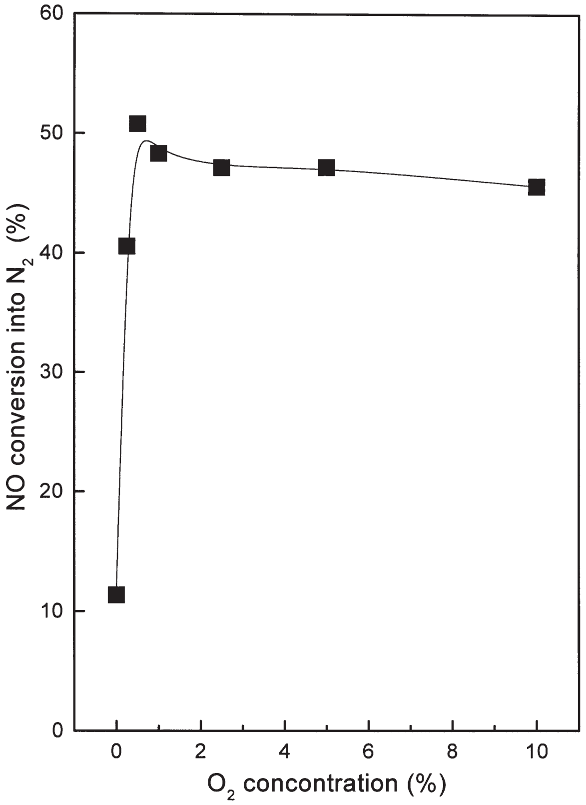

Figure 6. NO conversion as a function of O_2 concentration at 550 °C on Co-CLI catalyst. The reaction was run with a feed consisting of 1640 ppm NO and 1000 ppm CH_4 at a GHSV of 12 000 h^{-1}.

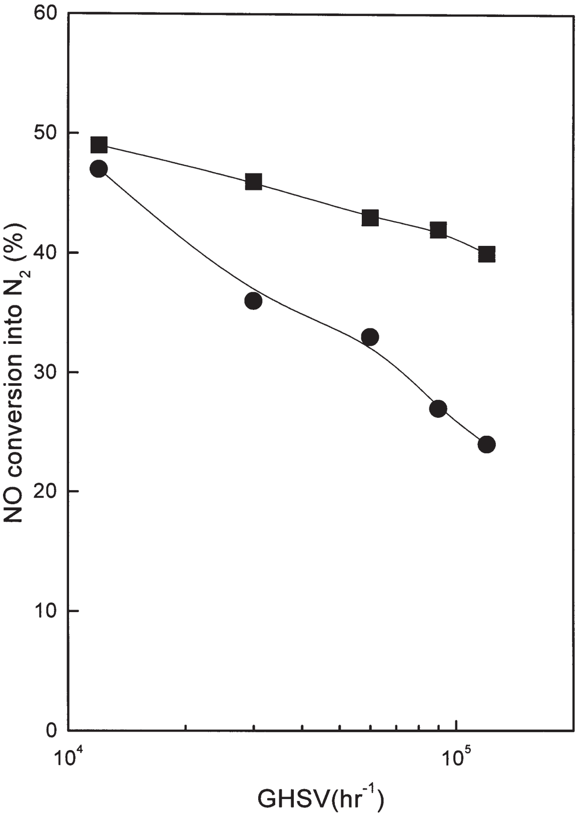

Figure 7. Variations in NO conversion on Co-FER (■) and Co-CLI (●) as a function of space velocity. The reactions were run with a feed containing 1640 ppm NO, 1000 ppm CH_4, and 2.5% O_2 at 500 °C (Co-FER) or 550 °C (Co-CLI).

10.0%. Therefore, it appears that the NO reduction on Co-CLI by CH_4 is not significantly affected by the presence of excess O_2 in the feed.

Figure 7 shows the effect of space velocity on the NO reduction activities of Co-FER and Co-CLI. It can be seen that the NO conversion on both catalysts decreases almost linearly with increasing space velocity. However, the extent of decrease in conversion is more severe on Co-CLI than on Co-FER. This is not unexpected because the diffusion of CH_4 with a kinetic diameter of 3.8 Å must be more restricted within the smaller and more elliptical 10-ring channels of Co-CLI. It has been speculated that the shape selectivity of zeolites used as supports for Co^{2+} ions is not crucial for the reduction of NO by CH_4 in excess O_2, due to the relatively small sizes of reactant molecules [23–25]. However, the results presented so far suggest that the suitable pore size for zeolite catalysts, as well as the proper siting and coordination of intrazeolitic Co^{2+} ions, may be required in achieving the high CH_4 selectivity for NO reduction together with the fast mass transfer of reactants. In this regard, we believe that one appropriate way to find an optimum zeolite-based catalyst for this reaction is to continually explore the potential of new medium-pore zeolites with an intersecting 10-ring and 8-ring channel system, e.g., ZSM-57 [32] and SUZ-4 [33], as hosts for Co^{2+} ions or other metal cations.

In summary, the catalytic results of this study demonstrate that cobalt species supported on synthetic clinoptilolite (Co-CLI) is an active catalyst for the reduction of NO with CH_4 in the presence of excess O_2. It is found that Co-CLI is more selective in the use of CH_4 for NO reduction than Co-ZSM-5 or Co-FER at $T \leqslant 450\,^{\circ}\mathrm{C}$, which can be related to its unique pore structure having the ability to effectively suppress CH_4 combustion and locate its Co^{2+} ions at the thermodynamically more stable sites in 8-ring channels.

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