

REACTION INTERMEDIATE OVER MORDENITE-TYPE ZEOLITE CATALYSTS FOR NO REDUCTION BY HYDROCARBONS

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Abstract – An infrared spectroscopic study has been made over mordenite-type zeolite catalysts prepared by the ion exchanging method to observe a surface species during the selective reduction of NO by hydrocarbons with and without H₂O. The strong absorptions at 2,274 and 2,325 cm⁻¹ were observed over HM and CuHM as well as over CuNZA catalysts, respectively after the reaction without H₂O, regardless of the types of reductant employed. It may be attributed to the isocyanate (-NCO) species formed on the catalyst surface which may be one of the most probable reaction intermediates for this reaction system. When H₂O was added to the feed gas stream, its formation on the synthetic mordenite catalysts such as HM and CuHM was significantly suppressed, but not for CuNZA catalyst. It agrees well with the fact that CuNZA catalyst exhibits a strong water tolerance for this reaction system. It also reveals that the formation of the -NCO species on the catalyst surface plays a crucial role for the maintenance of NO removal activity when H₂O exists in the feed gas stream.

Key words : NO Reduction, Mordenite, Isocyanate Species, FT-IR Spectroscopy, Hydrocarbon

INTRODUCTION

There have been many suggestions for the reaction mechanism of the selective reduction of NO by hydrocarbons and it is still under investigation. Recently, it has been extensively reviewed by Smits and Iwasawa [1995] as well as by Adelman et al. [1996]. Proposed reaction schemes for the reduction may be classified into four categories : (a) the formation of NO₂ from NO and O₂ as an initial reaction step, and then the reaction of NO₂ with hydrocarbons to produce N₂ [Yokoyama and Misono, 1994; Li et al., 1994; Guyon et al., 1996]; (b) the decomposition of NO into nitrogen and oxygen atoms on active reaction sites on the catalyst surface and the restoration of the sites into their initial state by hydrocarbons [Burch and Scire, 1994]; (c) the reduction of NO by a carbonaceous deposit produced from hydrocarbons [Obuchi et al., 1992]; and (d) the reduction of NO by a partially oxidized species from hydrocarbon and oxygen [Bennett et al., 1992].

Although (a) prevails as an initial reaction step for the reduction, the reaction intermediate, a complex of NO₂-hydrocarbon formed on the catalyst surface, was not clearly identified by a spectroscopic method. Burch and Scire [1994] proposed reaction mechanism (b) for NO removal reaction with CH₄ and C₂H₆ on ZSM-5 catalysts containing Rh, Pt, Co and Cu. However, it differs from the direct decomposition of NO without hydrocarbons which is successfully maintained by redox chemistry with the rapid desorption of oxygen produced from its decomposition [Valyon and Hall, 1993]. It may not

be feasible for H-zeolites which still exhibit high NO removal activity under SCR conditions with hydrocarbons [Iwamoto et al., 1993; Kim et al., 1995, 1997]. It should be noted that metal ionic sites on the catalyst surface are responsible for the catalytic decomposition of NO.

On the other hand, several kinds of reaction intermediates for NO reduction by hydrocarbons have been speculated as an evidence observed from spectroscopic or mass spectrometric studies. Surface NO_x species such as nitrosyls (M-NO), dinitrosyls [M-(NO)₂], nitrites (M-NO₂ or M-ONO) and nitrates (M-NO₃ or M-ONO₂) have been found upon the adsorption of NO_x on zeolite catalysts containing transition metal ions [Li et al., 1994; Valyon and Hall, 1993; Hoost et al., 1995; Hadjiiivanov et al., 1996; Hayes et al., 1996]. They have been regarded as plausible intermediates for the reduction of NO by hydrocarbons. The role of organic nitro- and nitrito-species on the catalyst surface was also examined by FT-IR studies [Smits and Iwasawa, 1995; Yokoyama and Misono, 1994; Li et al., 1994; Hayes et al., 1996]. The formation of isocyanate (-NCO) species on Al₂O₃-based catalysts was observed during NO removal reaction with hydrocarbons such as C₃H₆, C₂H₂ or n-C₇H₁₆ [Ukisu et al., 1993]. Surface N-containing compounds such as C₂N₂, -CN and -NCO along with organic nitro-groups are observed over Na- and Ce-exchanged ZSM-5 catalysts [Yokoyama and Misono, 1994]. Both surface nitrile and isocyanate compounds were also found over Cu-ZrO₂ catalyst for NO reduction by C₃H₆ [Li et al., 1995].

Based upon the reaction mechanisms and intermediates proposed for NO removal reaction, which of the reaction schemes listed from (a) to (d) plays a major role for the reduction is still controversial. All of them may be involved for this SCR

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technology using hydrocarbons as a reductant. More intensive study may be required to elucidate the reaction mechanism of this technology.

The effect of H_2O on the catalytic activity of mordenite-type zeolite catalysts such as HM, CuHM and CuNZA for the selective reduction of NO by hydrocarbons and the role of H_2O for the removal reaction has been extensively studied by Kim et al. [1997]. The role of a partially oxidized intermediate formed on the catalyst surface for NO removal reaction has been previously suggested [Kim et al., 1995]. In the present work, evidence was observed by *in situ* FT-IR spectroscopy as one of reaction intermediates on the surface of the zeolite catalysts to elucidate the effect of H_2O on NO removal activity.

EXPERIMENTAL

The synthetic mordenite (Zeolon 900Na) was obtained from PQ Corporation for the preparation of hydrogen mordenite (HM) and Cu-exchanged hydrogen mordenite (CuHM). CuNZA (Cu-exchanged natural zeolite) catalyst was also prepared by a natural zeolite mined from Youngil, Korea which contains mainly mordenite-type zeolite. The ion exchange method and physicochemical properties of the catalysts employed in the present study have been previously described elsewhere [Kim et al., 1995]. The copper contents of CuHM and CuNZA catalysts are 3.5 (Cu/Al=0.24) and 2.0 wt% (Cu/Al=0.22), respectively.

A reaction mixture including 500 ppm NO, 1,000 ppm C_2H_4 or 2,000 ppm C_3H_6 , 4.2 % O_2 and He (balance) was employed. To examine the effect of H_2O on the formation of a reaction intermediate during the course of reaction, 7.3 % H_2O was fed to the feed gas stream by bubbling of He into a water saturator with a small pore frit in addition to the reaction condition described as above. The details of the reaction conditions have been well described in previous work [Kim et al., 1997]. The self-supporting catalyst wafer (5-10 mg/cm²) was included in a laboratory-designed IR cell which is attachable not only to a high vacuum system maintained at about 10⁻⁶ mmHg by a turbomolecular pump (Leybold-Heraeus PT 150) but to a gas feeding system. After the catalyst wafer in the cell was pretreated at 550 °C for 2 h, the surface species formed on the catalyst surface during the reduction of NO by hydrocarbons with or without H_2O at 360 or 400 °C were examined at room temperature by a Perkin-Elmer 1800 FT-IR spectrophotometer with a spectral resolution of 4 cm⁻¹.

RESULTS AND DISCUSSION

1. Formation of Isocyanate Species for NO Reduction by HCs over Mordenites

Kim et al. [1995] reported recently a couple of catalytic systems which exhibit high NO reducing activity by hydrocarbons without H_2O : HM or CuHM catalyst employing C_2H_4 as a reductant and CuNZA catalyst with C_3H_6 . In addition, about 63 % of the initial NO conversion of HM and CuHM catalysts dropped immediately to 20 % of the conversion when 7.3 % H_2O was present in the feed gas stream, while a loss of NO conversion less than 10 % was observed for CuNZA catalyst, as shown in Fig. 1. In addition, CuHM catalyst re-

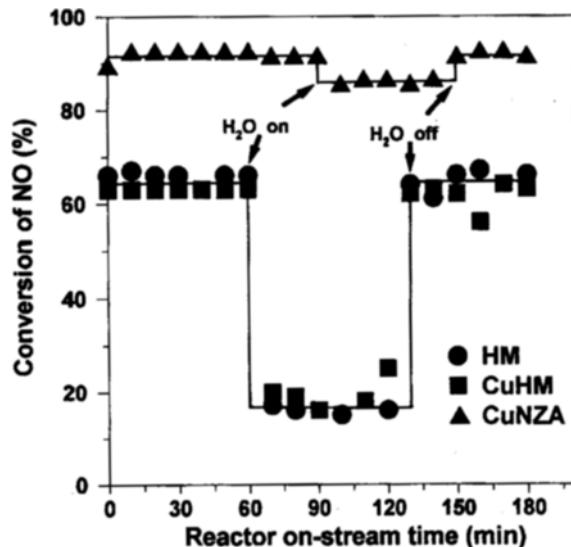


Fig. 1. Effect of H_2O on the deNO_x performance of mordenite-type zeolite catalysts.

Reaction condition: NO 500 ppm, C_2H_4 1,000 (HM and CuHM) or C_3H_6 2,000 ppm (CuNZA), O_2 4.2 %, H_2O 7.3% and T=360 (HM and CuHM) or 400 °C (CuNZA).

vealed higher water tolerance for NO reduction by C_2H_4 when H_2O is less than 7 % in the feed gas stream [Kim et al., 1997]. It is interesting to examine a reaction intermediate for the reaction system exhibiting the maintenance of NO removal activity with respect to the existence of H_2O in the feed gas stream. In the present study, a surface species formed on the catalyst surface during the course of the reduction with and without H_2O was observed.

Fig. 2 shows IR spectra of the catalysts before and after the reaction in the absence of H_2O . HM catalyst exposed to the reaction stream exhibited a strong absorption band at 2,274 cm⁻¹ and broad bands between 2,200 and 1,950 cm⁻¹. A similar peak at 2,275 cm⁻¹ was also observed for CuHM catalyst. However, the IR spectra of the catalyst in the absorption ranges lower than 2,200 cm⁻¹ are clearly different compared to those over HM catalyst, revealing a distinct peak at 1,900 cm⁻¹. CuNZA catalyst also shows the development of three bands in the wavenumber regions from 2,400 to 1,800 cm⁻¹, with maxima at 2,325, 2,032 and 1,903 cm⁻¹. None of these bands are observed for the fresh catalysts.

The formation of -NCO species has been observed for the reaction of NO and CO over supported noble metal catalysts: at 2,270 to 2,250 cm⁻¹ for Al_2O_3 as a support [Unland, 1973; Hecker and Bell, 1984] and at 2,320 to 2,180 cm⁻¹ for SiO_2 [Hecker and Bell, 1984]. Solymosi et al. [1978] also reported its absorption peak at a similar frequencies for Pt catalyst impregnated on supports such as Al_2O_3 , SiO_2 , TiO_2 and MgO . The IR band at 2,280 cm⁻¹ was also developed over H- and Pd-exchanged Y zeolites for the same reaction with the confirmation by the adsorption of isocyanic acid on the catalyst surface as a reference [Rasko and Solymosi, 1984].

Prominent IR absorptions at 2,270 to 2,230 cm⁻¹ by isocyanate species were also observed for NO reduction by hydrocarbons over SCR catalysts [Ukisu et al., 1993; Li et al., 1995].

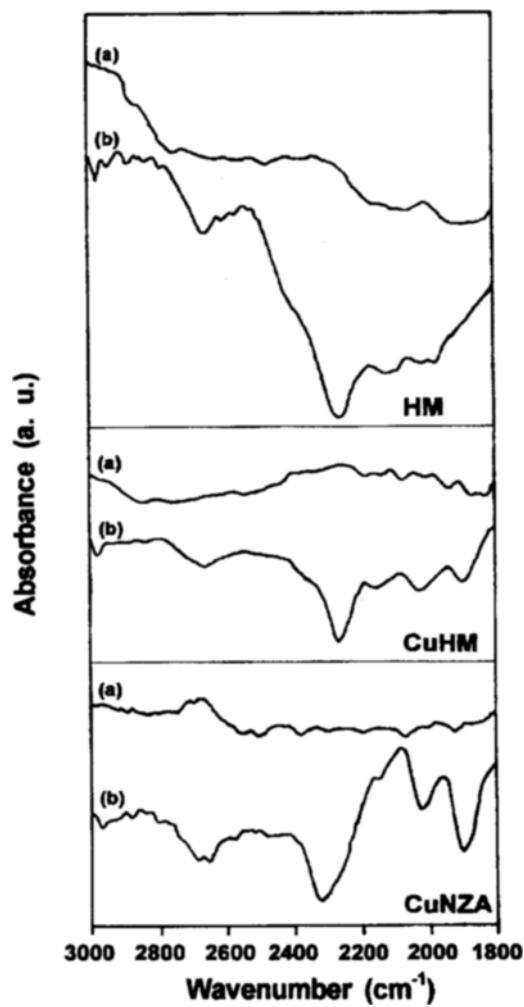


Fig. 2. IR spectra of mordenite-type zeolite catalysts: (a) before reaction; (b) after reaction without H_2O .

Reaction condition: NO 500 ppm, C_2H_6 1,000 (HM and CuHM) or C_3H_8 2,000 ppm (CuNZA), O_2 4.2% and $T = 360$ (HM and CuHM) or 400°C (CuNZA.)

Hayes et al. [1996] tentatively assigned the band at $2,260\text{ cm}^{-1}$ observed for the reduction of NO with C_3H_8 over CuZSM-5 catalyst to an organic nitrile species, while Hoost et al. [1995] to an isocyanate for a similar band at $2,295\text{ cm}^{-1}$. A stretching vibration of nitrile groups is also typical at about $2,290$ to $2,230\text{ cm}^{-1}$ [Chong and Curthoys, 1981]. This indicates that they may not be easily identified by IR, as discussed previously by Hayes et al. [1996]. However, not only was an unknown N-containing species containing C, N and O in a 1:1:1 ratio formed on Na- and Ce-exchanged ZSM-5 catalysts [Yokoyama and Misono, 1994], but the adsorption of isocyanic acid (HNCO) on CuZSM-5 catalyst also led to a strong absorption peak at $2,260\text{ cm}^{-1}$ [Hwang et al., 1996]. With the absorption band at $2,298\text{ cm}^{-1}$ for a CuZSM-5 catalyst adsorbing acetone oxime, Beutel et al. [1996] also detected a similar IR peak at $2,271\text{ cm}^{-1}$ when the catalyst was treated with aqueous NaNCO solution. Moreover, HCN and C_2N_2 chemisorbed on SiO_2 as SiCN and SiNC could be easily converted into SiNCO by heating in oxygen atmosphere, as previously reported by Morrow and Cody [1975].

Based upon the previous studies, the absorption bands at $2,274$ and $2,325\text{ cm}^{-1}$ observed in Fig. 2 may be attributed to the isocyanate species formed on the surface of the zeolite catalysts. The same species was also observed over CuZSM-5 catalyst for NO reduction by C_2H_6 , but not with C_2H_4 [Hwang et al., 1996]. However, its formation on the mordenite-type zeolite catalysts was observed, regardless of the types of reductant employed in the present study, which is also in good agreement with the IR study for NO reduction by C_2H_4 and C_3H_8 over CuZSM-5 catalyst [Radtke et al., 1995]. The band intensity of the -NCO species on the surface of CuZSM-5 catalyst notably decreased, when it contacted with a feed gas stream containing NO and O_2 at 350°C [Hwang et al., 1996]. This reveals that the species plays a crucial role for NO removal reaction with hydrocarbons. It indicates that the -NCO species formed on the catalyst surface becomes one of common observable surface intermediates for this reaction system.

In addition, the surface intermediates such as (di)nitrosyls, nitrites, nitrates, organic nitro- and nitrito-groups, isocyanate, and cyanide species over the catalysts for NO reduction by hydrocarbons might show a difference in catalytic reactivity during the course of the reaction [Hwang et al., 1996; Aylor et al., 1997; Misono et al., 1997]. Recently, Lobree et al. [1997] and Aylor et al. [1997] reported distinctive reactivity of isocyanate and cyanide species observed for steady-state reaction of NO with CH_4 over Co- and Mn-ZSM-5 catalysts, when these species have been exposed to NO_x or O_2 at the reaction temperature of 450°C . However, the reactivity of the surface species in this reaction system significantly depends not only on the reaction conditions such as reaction temperatures and concentrations of NO_x , O_2 or HCs, but also on the types of reducing agent and catalyst [Hwang et al., 1996; Aylor et al., 1997; Misono et al., 1997]. It should be noted that the formation of the -NCO species on the surface of mordenite-type zeolite catalysts was examined only for the experimental condition described in the present study. It may also be necessary to examine the low frequency regions from $1,345$ to $1,320\text{ cm}^{-1}$ as supporting evidence for the formation of the reaction intermediate by Raman shift minimizing the absorption of the zeolite itself.

When NO is adsorbed on the surface of Cu-exchanged zeolite catalysts, three major nitrosyl complexes such as $\text{Cu}^{2+}\text{-NO}$, $\text{Cu}^+\text{-NO}$ and $\text{Cu}^{2+}\text{-}(\text{NO})_2$ are commonly formed on the catalyst surface [Valyon and Hall, 1993; Cheung et al., 1996]. It is generally known that the surface NO_x species on the zeolite catalysts exhibit absorption bands at $1,895$ to $1,910\text{ cm}^{-1}$ [Valyon and Hall, 1993; Hoost et al., 1995; Hadjiiivanov et al., 1996; Hayes et al., 1996; Hwang et al., 1996; Cheung et al., 1996]. Therefore, the peaks at $1,900$ and $1,903\text{ cm}^{-1}$ over CuHM and CuNZA catalysts are primarily due to the formation of NO bonded [FSO1] to isolated Cu^{2+} sites on the catalyst surface. This is clear from the fact that no absorption at this wavenumber region occurred for the copper-free catalyst, HM. Note that both catalysts maintain less than 0.25 of Cu/Al molar ratio. The identification of the bands in the regions from $2,200$ to $1,950\text{ cm}^{-1}$, notably at $2,148$ and $2,030\text{ cm}^{-1}$ is less straightforward. These two bands are not primarily due to the adsorbed hydrocarbons on the catalyst surface which exhibit generally

absorption peaks at about 3,000, 1,660-1,600 and 1,000-650 cm^{-1} for =C-H and C=C groups. They may arise from carbonyl species on the catalyst surface.

2. Effect of H_2O on the Formation of Isocyanate Species

To examine the effect of H_2O on the formation of the -NCO species during the reduction of NO by hydrocarbons, the IR spectra of the three catalysts were examined in the presence of 7.3 % H_2O , as shown in Fig. 3. The absorption intensity of the -NCO species at 2,274 cm^{-1} decreased significantly for the synthetic mordenite catalysts, HM and CuHM, while a notable change was not found for CuNZA catalyst even with H_2O . The peaks between 2,200 and 1,950 cm^{-1} maintain their intensity, regardless of the presence of H_2O in the feed gas stream. Reduction of the -NCO band by H_2O adsorbed on the surface of Al_2O_3 -supported Cu-Cs oxide catalyst has been previously reported [Ukisu et al., 1993]. However, no difference in the peak intensity for the catalyst with gas phase water was observed compared to that of the hydrated catalyst. Significant formation of HCN, HCNO and C_2N_2 was also observed for less active catalysts at lower reaction temperatures [Yokoyama and Misono, 1994]. This suggests that the decomposition of the -NCO species and/or its reaction with NO_x , O_2 and/or hydrocarbons to convert final products may be the rate-controlling step for this reaction system.

Less than 10 % of the loss of NO removal activity for CuNZA catalyst was found even with 7.3 % H_2O , but HM and CuHM catalysts exhibited reduction of more than 45 % with the same water content in the feed gas stream, as shown in Fig. 1. This agrees well with the dramatic loss of the absorp-

tion band of the -NCO species on the surface of the synthetic mordenite catalysts. The significant loss of the de NO_x efficiency of the zeolite catalysts for NO removal reaction in the presence of H_2O is primarily due to the competitive adsorptions of NO and H_2O on the catalyst surface as well as of hydrocarbons and H_2O [Kim et al., 1997]. The reduction of NO removal activity by H_2O , however, was apparently negligible for CuNZA catalyst. It should be noted that the adsorption capacity of NO and hydrocarbons on CuNZA catalyst was also maintained even with H_2O [Kim et al., 1997]. This supports readily that the addition of H_2O to the catalyst surface does not suppress the formation of the -NCO species as observed in Fig. 3. Based upon the distinctive decrease in the absorption intensity of the -NCO species by H_2O , it is probably one of the most important reaction intermediates for NO reduction by hydrocarbons over the mordenite-type zeolite catalysts. It may also be a reason why CuNZA catalyst exhibits the strong water tolerance found in the previous study [Kim et al., 1997]. In addition, it may be necessary to examine an alteration of the absorption intensity of the -NCO species on the catalyst surface with respect to the content of water in the feed gas stream as well as the reaction temperature.

CONCLUSIONS

A surface isocyanate species was formed on the mordenite-type zeolite catalysts for the reduction of NO by hydrocarbons, regardless of the types of reductant employed in the present study. It is one of the most suspected reaction intermediates for NO removal reaction over the catalysts. The formation of -NCO species on the catalyst surface is critical for the maintenance of NO removal activity in wet feed gas stream.

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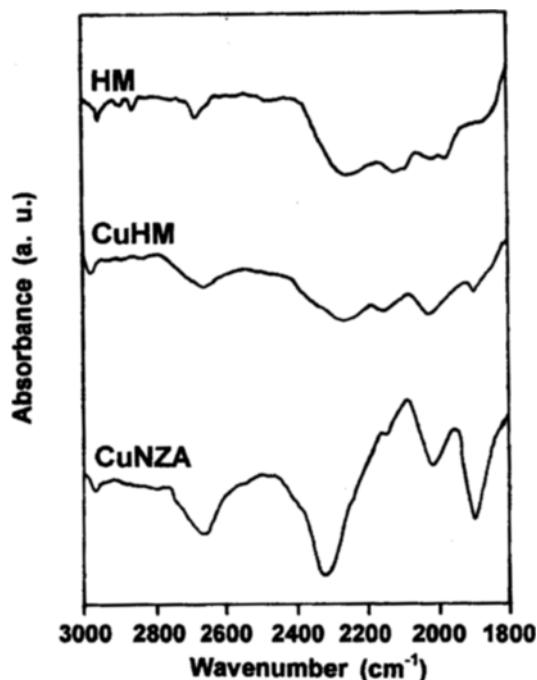


Fig. 3. IR spectra of mordenite-type zeolite catalysts after reaction with H_2O .

Reaction condition: NO 500 ppm, C_2H_4 1,000 (HM and CuHM) or C_3H_8 2,000 ppm (CuNZA), O_2 4.2 %, H_2O 7.3 % and $T=360$ (HM and CuHM) or 400°C (CuNZA).

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