

## 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 H<sub>2</sub>O. The strong absorptions at 2,274 and 2,325 cm<sup>-1</sup> were observed over HM and CuHM as well as over CuNZA catalysts, respectively after the reaction without H<sub>2</sub>O, 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 H<sub>2</sub>O 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 H<sub>2</sub>O 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 NO<sub>2</sub> from NO and O<sub>2</sub> as an initial reaction step, and then the reaction of NO<sub>2</sub> with hydrocarbons to produce N<sub>2</sub> [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 NO<sub>2</sub>-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 CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> 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<sub>x</sub> species such as nitrosyls (M-NO), dinitrosyls [M-(NO)<sub>2</sub>], nitrites (M-NO<sub>2</sub> or M-ONO) and nitrates (M-NO<sub>3</sub> or M-ONO<sub>2</sub>) have been found upon the adsorption of NO<sub>x</sub> on zeolite catalysts containing transition metal ions [Li et al., 1994; Valyon and Hall, 1993; Hoost et al., 1995; Hadjiivanov 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 Al<sub>2</sub>O<sub>3</sub>-based catalysts was observed during NO removal reaction with hydrocarbons such as C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>2</sub> or n-C<sub>7</sub>H<sub>16</sub> [Ukisu et al., 1993]. Surface N-containing compounds such as C<sub>2</sub>N<sub>2</sub>, -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-ZrO<sub>2</sub> catalyst for NO reduction by C<sub>3</sub>H<sub>8</sub> [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/cm<sup>2</sup>) 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<sup>-1</sup>.

## 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-

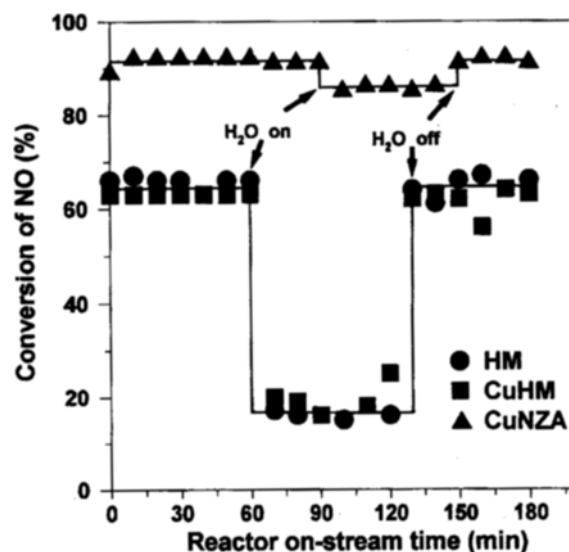


Fig. 1. Effect of  $H_2O$  on the deNO<sub>x</sub> performance of mordenite-type zeolite catalysts.

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<sup>-1</sup> and broad bands between 2,200 and 1,950 cm<sup>-1</sup>. A similar peak at 2,275 cm<sup>-1</sup> was also observed for CuHM catalyst. However, the IR spectra of the catalyst in the absorption ranges lower than 2,200 cm<sup>-1</sup> are clearly different compared to those over HM catalyst, revealing a distinct peak at 1,900 cm<sup>-1</sup>. CuNZA catalyst also shows the development of three bands in the wavenumber regions from 2,400 to 1,800 cm<sup>-1</sup>, with maxima at 2,325, 2,032 and 1,903 cm<sup>-1</sup>. 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<sup>-1</sup> for  $Al_2O_3$  as a support [Unland, 1973; Hecker and Bell, 1984] and at 2,320 to 2,180 cm<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> by isocyanate species were also observed for NO reduction by hydrocarbons over SCR catalysts [Ukisu et al., 1993; Li et al., 1995].

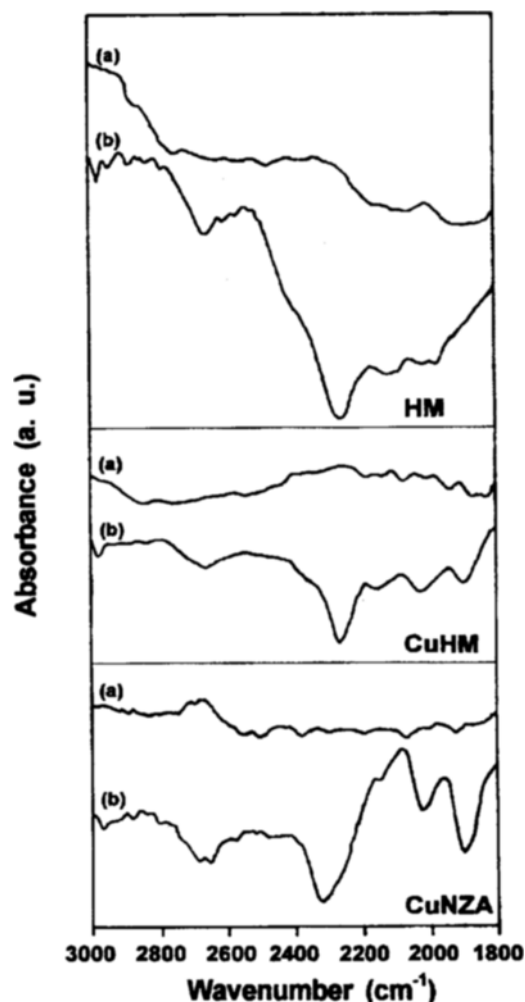


Fig. 2. IR spectra of mordenite-type zeolite catalysts: (a) before reaction; (b) after reaction without  $\text{H}_2\text{O}$ .

Reaction condition: NO 500 ppm,  $\text{C}_2\text{H}_4$  1,000 (HM and CuHM) or  $\text{C}_3\text{H}_6$  2,000 ppm (CuNZA),  $\text{O}_2$  4.2 % and  $T=360$  (HM and CuHM) or  $400^\circ\text{C}$  (CuNZA.)

Hayes et al. [1996] tentatively assigned the band at  $2,260\text{ cm}^{-1}$  observed for the reduction of NO with  $\text{C}_3\text{H}_6$  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  $\text{C}_2\text{N}_2$  chemisorbed on  $\text{SiO}_2$  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  $\text{C}_3\text{H}_6$ , but not with  $\text{C}_2\text{H}_4$  [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  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  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  $\text{O}_2$  at  $350^\circ\text{C}$  [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  $\text{CH}_4$  over Co- and Mn-ZSM-5 catalysts, when these species have been exposed to  $\text{NO}_x$  or  $\text{O}_2$  at the reaction temperature of  $450^\circ\text{C}$ . 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  $\text{NO}_x$ ,  $\text{O}_2$  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  $\text{Cu}^{2+}\text{-(NO)}_2$  are commonly formed on the catalyst surface [Valyon and Hall, 1993; Cheung et al., 1996]. It is generally known that the surface  $\text{NO}_x$  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; Hadjiivanov 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  $\text{Cu}^{2+}$  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  $\text{cm}^{-1}$  for  $=\text{C}-\text{H}$  and  $\text{C}=\text{C}$  groups. They may arise from carbonyl species on the catalyst surface.

## 2. Effect of $\text{H}_2\text{O}$ on the Formation of Isocyanate Species

To examine the effect of  $\text{H}_2\text{O}$  on the formation of the  $-\text{NCO}$  species during the reduction of  $\text{NO}$  by hydrocarbons, the IR spectra of the three catalysts were examined in the presence of 7.3 %  $\text{H}_2\text{O}$ , as shown in Fig. 3. The absorption intensity of the  $-\text{NCO}$  species at 2,274  $\text{cm}^{-1}$  decreased significantly for the synthetic mordenite catalysts, HM and CuHM, while a notable change was not found for CuNZA catalyst even with  $\text{H}_2\text{O}$ . The peaks between 2,200 and 1,950  $\text{cm}^{-1}$  maintain their intensity, regardless of the presence of  $\text{H}_2\text{O}$  in the feed gas stream. Reduction of the  $-\text{NCO}$  band by  $\text{H}_2\text{O}$  adsorbed on the surface of  $\text{Al}_2\text{O}_3$ -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  $\text{HCN}$ ,  $\text{HCNO}$  and  $\text{C}_2\text{N}_2$  was also observed for less active catalysts at lower reaction temperatures [Yokoyama and Misono, 1994]. This suggests that the decomposition of the  $-\text{NCO}$  species and/or its reaction with  $\text{NO}_x$ ,  $\text{O}_2$  and/or hydrocarbons to convert final products may be the rate-controlling step for this reaction system.

Less than 10 % of the loss of  $\text{NO}$  removal activity for CuNZA catalyst was found even with 7.3 %  $\text{H}_2\text{O}$ , 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  $-\text{NCO}$  species on the surface of the synthetic mordenite catalysts. The significant loss of the  $\text{deNO}_x$  efficiency of the zeolite catalysts for  $\text{NO}$  removal reaction in the presence of  $\text{H}_2\text{O}$  is primarily due to the competitive adsorptions of  $\text{NO}$  and  $\text{H}_2\text{O}$  on the catalyst surface as well as of hydrocarbons and  $\text{H}_2\text{O}$  [Kim et al., 1997]. The reduction of  $\text{NO}$  removal activity by  $\text{H}_2\text{O}$ , however, was apparently negligible for CuNZA catalyst. It should be noted that the adsorption capacity of  $\text{NO}$  and hydrocarbons on CuNZA catalyst was also maintained even with  $\text{H}_2\text{O}$  [Kim et al., 1997]. This supports readily that the addition of  $\text{H}_2\text{O}$  to the catalyst surface does not suppress the formation of the  $-\text{NCO}$  species as observed in Fig. 3. Based upon the distinctive decrease in the absorption intensity of the  $-\text{NCO}$  species by  $\text{H}_2\text{O}$ , it is probably one of the most important reaction intermediates for  $\text{NO}$  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  $-\text{NCO}$  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  $\text{NO}$  by hydrocarbons, regardless of the types of reductant employed in the present study. It is one of the most suspected reaction intermediates for  $\text{NO}$  removal reaction over the catalysts. The formation of  $-\text{NCO}$  species on the catalyst surface is critical for the maintenance of  $\text{NO}$  removal activity in wet feed gas stream.

## REFERENCES

- Adelman, B. J., Beutel, T., Lei, G.-D. and Sachtler, W. M. H., "On the Mechanism of Selective  $\text{NO}_x$  Reduction with Alkanes over Cu/ZSM-5," *Appl. Catal. B*, **11**, L1 (1996).
- Aylor, A. W., Lobree, L. J., Reimer, J. A. and Bell, A. T., "NO Adsorption, Desorption, and Reduction by  $\text{CH}_4$  over Mn-ZSM-5," *J. Catal.*, **170**, 390 (1997).
- Bennett, C. J., Bennett, P. S., Golunski, S. E., Hayes, J. W. and Walker, A. P., "Selective Reduction of Nitrogen Oxides under Oxidizing Exhaust-Gas Conditions," *Appl. Catal. A*, **86**, L1 (1992).
- Beutel, T., Adelman, B. J. and Sachtler, W. M. H., "Potential Reaction Paths in  $\text{NO}_x$  Reduction over Cu/ZSM-5," *Catal. Lett.*, **37**, 125 (1996).
- Burch, R. and Scire, S., "Selective Catalytic Reduction of Nitric Oxide with Ethane and Methane on Some Metal Exchanged ZSM-5 Zeolites," *Appl. Catal. B*, **3**, 295 (1994) and therein references.
- Cheung, T., Bhargava, S. K., Hobday, M. and Foger, K., "Adsorption of  $\text{NO}$  on Cu Exchanged Zeolites, a FTIR Study: Effects of Cu Levels,  $\text{NO}$  Pressure, and Catalyst Pretreatment," *J. Catal.*, **158**, 301 (1996).
- Chong, P. J. and Curthoys, G., "Infrared Spectroscopic Study of Acrylonitrile Adsorbed on Mordenite Zeolites," *J. Chem.*

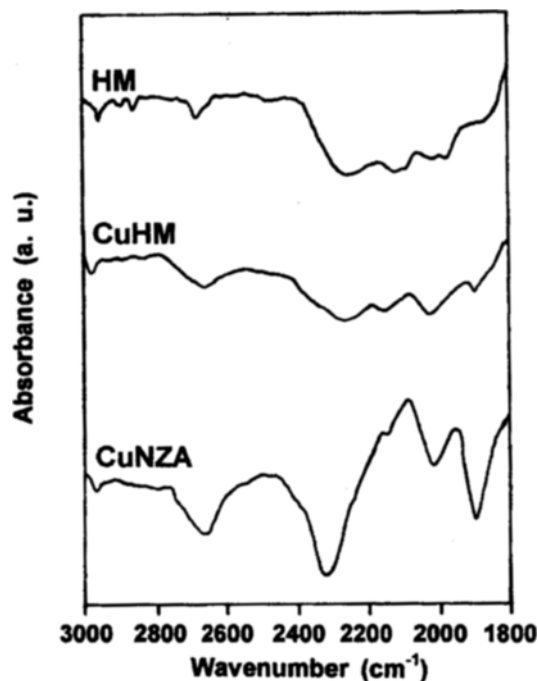


Fig. 3. IR spectra of mordenite-type zeolite catalysts after reaction with  $\text{H}_2\text{O}$ .

Reaction condition:  $\text{NO}$  500 ppm,  $\text{C}_2\text{H}_4$  1,000 (HM and CuHM) or  $\text{C}_3\text{H}_6$  2,000 ppm (CuNZA),  $\text{O}_2$  4.2 %,  $\text{H}_2\text{O}$  7.3 % and  $T=360$  (HM and CuHM) or  $400^\circ\text{C}$  (CuNZA).

- Soc., Faraday Trans. I*, **77**, 1639 (1981).
- Guyon, M., Le Chanu, V., Gilot, P., Kessler, H. and Prado, G., "Experimental Study of the Formation and the Reaction of an Intermediate during the Lean NO<sub>x</sub> Reaction over Cu-ZSM-5," *Appl. Catal. B*, **8**, 183 (1996).
- Hadjiivanov, K., Klissurski, D., Ramis, G. and Busca, G., "Fourier Transform IR Study of NO<sub>x</sub> Adsorption on a CuZSM-5 DeNO<sub>x</sub> Catalyst," *Appl. Catal. B*, **7**, 251 (1996).
- Hay, W., Joyner, R. W. and Shpiro, S., "Infrared Spectroscopy Studies of the Mechanism of the Selective Reduction of NO<sub>x</sub> over Cu-ZSM-5 Catalysts," *Appl. Catal. B*, **8**, 343 (1996).
- Hecker, W. C. and Bell, A. T., "Infrared Observations of Rh-NCO and Si-NCO Species Formed during the Reduction of NO by CO over Silica-Supported Rhodium," *J. Catal.*, **85**, 389 (1984) and therein references.
- Hoost, T. E., Laframboise, K. A. and Otto, K., "Co-adsorption of Propene and Nitrogen Oxides on Cu-ZSM-5: A FTIR Study," *Appl. Catal. B*, **7**, 79 (1995).
- Hwang, I. C., Kim, D. H. and Woo, S. I., "The Existence of Dual Cu Site Involved in the Selective Catalytic Reduction of NO with Propene on Cu/ZSM-5," *Catal. Lett.*, **42**, 177 (1996).
- Iwamoto, M. and Mizuno, N., "NO<sub>x</sub> Emission Control in Oxygen-Rich Exhaust through Selective Catalytic Reduction by Hydrocarbon," *J. Auto. Eng.*, **207**, 23 (1993) and therein references.
- Kim, M. H., Nam, I.-S. and Kim, Y. G., (a) "Selective Reduction of Nitrogen Oxide by Hydrocarbons over Mordenite-Type Zeolite Catalysts," *Appl. Catal. B*, **6**, 297 (1995); (b) "Water Tolerance of Mordenite-type Zeolite Catalysts for Selective Reduction of Nitric Oxide by Hydrocarbons," *Appl. Catal. B*, **12**, 125 (1997).
- Li, C., Bethke, K. A., Kung, H. H. and Kung, M. C., "Detection of Surface CN and NCO Species as Possible Reaction Intermediates in Catalytic Lean NO<sub>x</sub> Reduction," *J. Chem. Soc., Chem. Commun.*, 813 (1995).
- Li, Y., Slager, T. L. and Armor, J. N., "Selective Reduction of NO<sub>x</sub> by Methane on Co-Ferrierites. II. Catalyst Characterization," *J. Catal.*, **150**, 388 (1994) and therein references.
- Lobree, L. J., Aylor, A. W., Reimer, J. A. and Bell, A. T., "Role of Cyanide Species in the Reduction of NO by CH<sub>4</sub> over Co-ZSM-5," *J. Catal.*, **169**, 188 (1997).
- Misono, M., Hirao, Y. and Yokoyama, C., "Reduction of Nitrogen Oxides with Hydrocarbons Catalyzed by Bifunctional Catalysts," *Catal. Today*, **38**, 157 (1997).
- Morrow, B. A. and Cody, I. A., "Infrared Studies of Reactions on Oxide Surfaces, Part 3. HCN and C<sub>2</sub>N<sub>2</sub> on Silica," *J. Chem. Soc., Faraday Trans. I*, **71**, 1021 (1975).
- Obuchi, A., Ogata, A., Mizuno, K., Ohi, A., Nakamura, M. and Ohuchi, H., "Mechanism of Selective Catalytic Reduction of Nitrogen Monoxide by Organic Compounds," *J. Chem. Soc., Chem. Commun.*, 247 (1992).
- Radtke, F., Koeppe, R. A. and Baiker, A., "Formation of HNCO during Catalytic Reduction of NO<sub>x</sub> with Olefins over Cu/ZSM-5," *J. Chem. Soc., Chem. Commun.*, 427 (1995).
- Rasko, J. and Solymosi, F., "NO+CO Interaction and NCO Formation on PdY Zeolite Studied by Infrared Spectroscopy," *J. Chem. Soc., Faraday Trans. I*, **80**, 1841 (1984).
- Smits, R. H. H. and Iwasawa, Y., "Reaction Mechanisms for the Reduction of Nitric Oxide by Hydrocarbons on Cu-ZSM-5 and Related Catalysts," *Appl. Catal. B*, **6**, L201 (1995).
- Solymosi, F., Volgyesi, L. and Sarkany, J., "The Effect of the Support on the Formation and Stability of Surface Isocyanate on Platinum," *J. Catal.*, **54**, 336 (1978).
- Ukisu, Y., Sato, S., Abe, A. and Yoshida, K., "Possible Role of Isocyanate Species in NO<sub>x</sub> Reduction by Hydrocarbons over Copper-Containing Catalysts," *Appl. Catal. B*, **2**, 147 (1993) and therein references.
- Unland, M. L., (a) "Isocyanate Intermediates in the Reaction of NO and CO over Noble Metal Catalysts," *J. Catal.*, **31**, 459 (1973); (b) "Isocyanate Intermediates in the Reaction NO+CO over a Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst," *J. Phys. Chem.*, **77**, 1952 (1973).
- Valyon, J. and Hall, W. K., "Studies of the Surface Species Formed from NO on Copper Zeolites," *J. Phys. Chem.*, **97**, 1204 (1993) and therein references.
- Yokoyama, C. and Misono, M., "Catalytic Reduction of Nitrogen Oxides by Propene in the Presence of Oxygen over Cerium Ion-Exchanged Zeolites," *J. Catal.*, **150**, 9 (1994).