

Formation of isocyanate species on the surface of mordenite-type zeolite catalysts for the reduction of NO by hydrocarbons with H₂O

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Surface isocyanate species with IR bands at 2274 and 2325 cm⁻¹ play a crucial role for the maintenance of the water tolerance of HM, CuHM and CuNZA catalysts for NO reduction by hydrocarbons in the presence of H₂O.

Several reaction intermediates for the selective reduction of NO by hydrocarbons have been suggested.¹⁻⁷ However, their significance during the course of the reaction is still under investigation. 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 the surface of zeolite catalysts containing transition metal ions¹⁻⁴ and have been regarded as plausible intermediates for this reaction system. The role of organic nitro- and nitrito-species on the catalyst surface was also examined by FTIR studies.^{1,4,5} The formation of isocyanate species (–NCO) on Al₂O₃-based catalysts was observed during NO removal reaction with hydrocarbons containing C₃H₆, C₂H₂ or *n*-C₇H₁₆.⁶ N-containing surface compounds such as C₂N₂, CN and NCO along with organic nitro-groups are observed over Na- and Ce-exchanged ZSM-5 catalysts.⁵ Both surface nitrile and isocyanate compounds were also found over Cu–ZrO₂ catalyst for NO reduction by C₃H₆.⁷ However, which of the proposed intermediates plays a major role for this reaction system is still controversial.

Kim *et al.*^{8a} recently reported a couple of catalytic systems exhibiting high NO removal activity: HM or CuHM catalyst employing C₂H₄ as a reductant and CuNZA catalyst with C₃H₆. The initial NO conversion of 63% of HM and CuHM catalysts immediately dropped to 20% conversion when 7.3% H₂O was present in the feed gas stream, while a loss of NO conversion of < 10% was observed for the CuNZA catalyst.^{8b} In the present study, it was of interest to examine from the viewpoint of reaction intermediates why the latter catalytic system exhibits stable deNO_x activity maintenance in the presence of H₂O in the feed gas stream while the former does not.

The preparation procedures and physicochemical properties of the mordenite-type zeolite catalysts HM, CuHM and CuNZA employed in this study have been previously described in detail elsewhere.⁸ The copper contents of CuHM and CuNZA catalysts are 3.5 (Cu/Al = 0.24) and 2.0 wt.% (Cu/Al = 0.22), respectively. When the reaction mixture including 500 ppm of NO, 1000 ppm of C₂H₄ or 2000 ppm of C₃H₆ and 4.2% of O₂ was admitted onto the self-supporting catalyst wafers pretreated at 550 °C for 2 h in a laboratory designed IR cell, the surface species formed on the catalyst surface during the reduction with or without H₂O at 360 or 400 °C were examined by *in situ* FTIR spectroscopy at room temperature.

Fig. 1 shows IR spectra before and after the reaction in the absence of H₂O. The HM catalyst after reaction exhibited a strong absorption band at 2274 cm⁻¹ and broad bands between 2200 and 1950 cm⁻¹. A similar peak at 2275 cm⁻¹ was also observed for the CuHM catalyst. However, the IR spectra of the catalyst in the absorption range < 2200 cm⁻¹ are clearly different compared to those over the HM catalyst, revealing a distinct peak at 1900 cm⁻¹. The CuNZA catalyst also shows the

development of three bands in the wavenumber region 2400–1800 cm⁻¹, with maxima at 2325, 2032 and 1903 cm⁻¹. None of these bands are observed for the catalysts before the reaction.

The formation of isocyanate (–NCO) species has been observed for the reaction of NO and CO over supported noble metal catalysts: at 2270–2250 cm⁻¹ for Al₂O₃⁹ and 2320–2180 cm⁻¹ for SiO₂^{9,10} as a support. Prominent IR absorptions at 2270–2230 cm⁻¹ of isocyanate species were also observed for NO reduction by hydrocarbons over SCR catalysts.^{6,7} Hayes *et al.*⁴ tentatively assigned the band at 2260 cm⁻¹ observed for the reduction of NO with C₃H₆ over CuZSM-5 catalyst to an organic nitrile species, while Hoost *et al.*³ suggested isocyanate for a similar band at 2295 cm⁻¹. An unassigned N-containing species containing C, N and O in a 1 : 1 : 1 ratio was formed on Na- and Ce-exchanged ZSM-5 catalysts⁵ whereas the adsorption of isocyanic acid (HNCO) on CuZSM-5 catalyst led to a strong absorption peak at 2260 cm⁻¹.¹¹ With the absorption band at 2298 cm⁻¹ for a CuZSM-5 catalyst adsorbing acetone oxime, Beutel *et al.*¹² also observed a similar IR peak at 2271 cm⁻¹ when the catalyst was treated with an aqueous NaNCO solution. Moreover, HCN and C₂N₂ chemisorbed on SiO₂ as SiCN and SiNC could be easily converted into SiNCO by heating in an oxygen atmosphere, as previously reported by Morrow and Cody.¹³

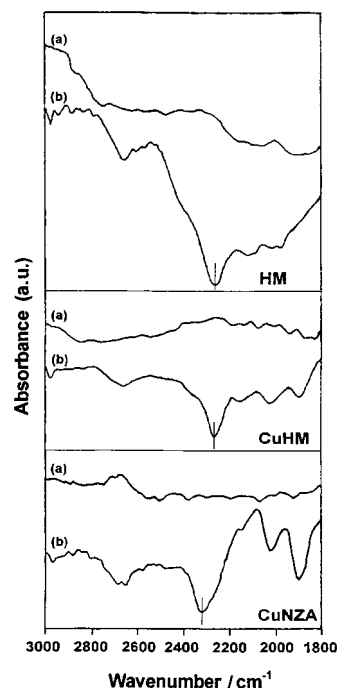


Fig. 1 IR spectra of mordenite-type zeolite catalysts: (a) before reaction; (b) after reaction without H₂O. Reaction conditions: NO 500 ppm, C₂H₄ 1000 (HM and CuHM) or C₃H₆ 2000 ppm (CuNZA), O₂ 4.2% and *T* = 360 (HM and CuHM) or 400 °C (CuNZA).

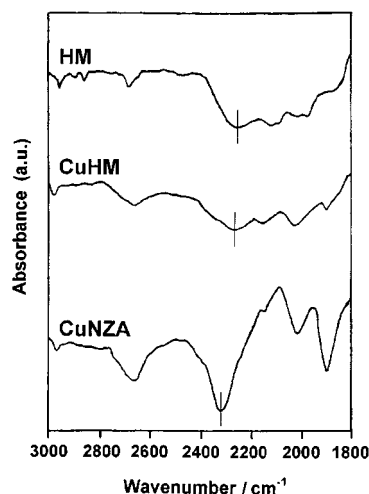


Fig. 2 IR spectra of mordenite-type zeolite catalysts after reaction with H₂O. Reaction conditions: NO 500 ppm, C₂H₄ 1000 (HM and CuHM) or C₃H₆ 2000 ppm (CuNZA), O₂ 4.2%, H₂O 7.3% and *T* = 360 (HM and CuHM) or 400 °C (CuNZA).

Based upon the previous studies, the absorption bands at 2274 and 2325 cm⁻¹ (Fig. 1) may be attributed to isocyanate species formed on the surface of the zeolite catalysts. The same species was also observed over CuZSM-5 catalyst for NO reduction by C₃H₆, but not with C₂H₄.¹¹ 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 C₂H₄ and C₃H₆ over CuZSM-5.¹⁴

Three major nitrosyl complexes such as Cu²⁺-NO, Cu⁺-NO and Cu²⁺-(NO)₂ are commonly observed for Cu-exchanged zeolites upon the adsorption of NO.^{2,15} It is generally known that the surface NO_x species on the zeolite catalysts exhibit absorption bands at 1895–1910 cm⁻¹.^{2–4,11} Therefore, the peaks at 1900 and 1903 cm⁻¹ over CuHM and CuNZA catalysts are primarily due to the formation of NO bonded to isolated Cu²⁺ sites on the catalyst surface. This is clear from the fact that no absorption in this wavenumber region occurred for the copper-free catalyst, HM. The identification of the bands in the region 2200–1950 cm⁻¹, notable at 2148 and 2030 cm⁻¹, is less straightforward; they may arise from carbonyl species formed on the catalyst surface.

To examine the effect of H₂O 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% H₂O, as shown in Fig. 2. The absorption intensity of the -NCO species at ca. 2274 cm⁻¹ significantly decreased for the synthetic mordenite catalysts, HM and CuHM in the presence of water, while no notable change was found for the CuNZA catalyst. However, the peaks between 2200 and 1950 cm⁻¹ still maintain their intensity, regardless of the presence of H₂O in the feed gas stream. Reduction of the -NCO band by H₂O adsorbed on the surface of Al₂O₃-supported Cu-Cs oxide catalyst has

also been reported.⁶ However, no difference in the peak intensities for the catalyst exposed to gas phase water and for the hydrated catalyst was observed.

HM and CuHM catalysts exhibited a loss of NO removal activity of >45% with 7.3% of H₂O in the feed gas stream^{8b} which is in accord with the dramatic reduction of the absorption band of the -NCO species on the surface of the catalysts. The significant loss of the deNO_x efficiency of the catalysts for the NO removal reaction in the presence of H₂O is primarily due to the competitive adsorption of NO and H₂O on the catalyst surface as well as of hydrocarbons and H₂O.^{8b} The alteration of NO removal activity by H₂O however, was apparently negligible for the CuNZA catalyst. It should be noted that the adsorption capacity of NO and hydrocarbons on CuNZA catalyst was also maintained with H₂O in the feed gas stream.^{8b} This indicates that the feed of H₂O to the catalyst surface does not suppress the formation of the reaction intermediate on the catalyst surface (see Fig. 2) and may be why the CuNZA catalyst exhibits the strong water tolerance found in the previous study.^{8b}

In conclusion, a surface isocyanate species was formed on mordenite-type zeolite catalysts for the reduction of NO by hydrocarbons, regardless of the reductant employed. This indicates that the species plays a crucial role for NO removal reaction with hydrocarbons over the catalysts. The formation of -NCO species on the catalyst surface is also critical for the maintenance of NO removal activity when H₂O is present in the feed gas stream.

Notes and References

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