

탄화수소에 의한 NO 제거 반응에서 물에 의해 활성저하되는
구리이온이 교환된 모더나이트형 제올라이트 촉매의 특성

김문현, 남인식, 김영걸

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Characteristics of Copper Ion-Exchanged Mordenite-Type Zeolite Catalysts
Deactivated by Water for Selective Reduction of NO_x by Hydrocarbons

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INTRODUCTION

Transition metal ion-exchanged zeolites or metal-supported catalysts have been reported to be quite effective for the selective reduction of NO_x with hydrocarbons[1]. Since the most of flue gas containing NO also comprises SO₂ and H₂O, their tolerance is required for the application of their process to a commercial unit. However, in the previous reports, SO₂ in the feed stream showed a moderate poisoning effect[3, 4], whereas H₂O had especially a strong poisoning effect even with the trace of its contents [1 - 7]. Especially, the deactivation of SCR catalysts using hydrocarbons is not well understood in the presence of water.

Water tolerance of copper ion-exchanged natural zeolite(CuNZA), mainly mordenite type zeolite has been recently observed to be much better than that of synthetic zeolite(HM and CuHM) for NO reduction by propene[8]. In this study, the cause of the deterioration of the catalyst activity by water for this catalytic system has been examined.

EXPERIMENTAL

HM, CuHM, and CuNZA catalysts were prepared according to conventional ion-exchanged methods. The copper contents of CuHM and CuNZA catalysts are 3.5 and 1.8wt.%, respectively. For the activity tests of the catalysts in a fixed-bed flow reactor, the mixture of gases containing 500ppm of NO, 1,000ppm of C₂H₄ or 2,000ppm of C₃H₆, 4.2% of O₂ and 0 to 17% of H₂O was used.

For the examination of the surface hydrophobicity of the catalysts prepared in this study, temperature-programmed desorption(TPD) of water vapor was performed. Both simultaneous adsorption of NO and water on the catalyst surface and the product distributions of NO reduction in the presence of water were examined. The optical reflectance spectra in the near infrared visible region were observed by BOMEM DA series interferometric spectrophotometer equipped with a silicon u.v. detector. The

experimental spectra were transformed with the Kubelka-Munk equation. To characterize adsorption of the hydrocarbons over CuNZA catalysts, their adsorption isotherms and chemisorption were made by a volumetric BET method.

RESULTS and DISCUSSION

Figure 1 shows the water tolerances of HM, CuHM and CuNZA catalyst. CuHM shows milder deactivation than HM, but both catalysts are definitely deactivated by water contained in the feed gas stream. However, CuNZA catalyst shows strong tolerance even with 16% of water contents. Copper-free catalyst is more easily deactivated by water than copper containing catalysts. In addition, propene is a good reductant from the view point of the activity loss by water.

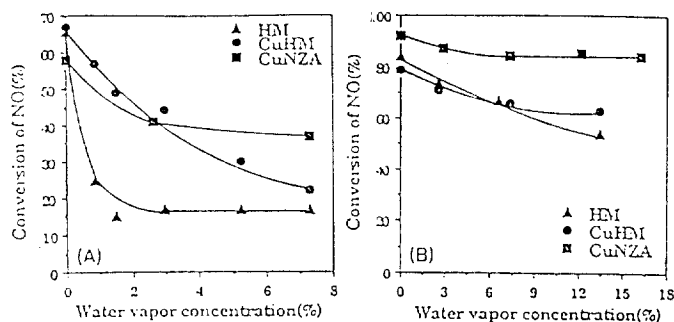


Fig. 1 Water tolerance of the catalysts. Reaction condition : (A) NO 500ppm, C_2H_2 1,000ppm, O_2 4.2%, and $T=360^\circ C$; (B) NO 500ppm, C_3H_6 2,000ppm, O_2 4.2%, and $T=400^\circ C$.

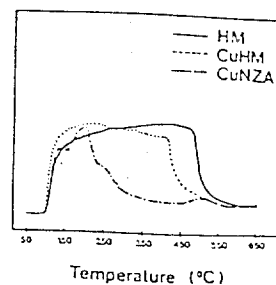


Fig. 2 TPD of water for the catalysts. The ramping rate was $10^\circ C/min$, and the carrier rate (He) was $40cm^3/min$.

The adsorption capacity and strength of water for HM catalyst is higher than for CuHM catalyst as shown in Fig. 2. However, CuNZA catalyst is most hydrophobic among the catalysts tested in this study, although it exhibits three distinctive desorption peaks. The deteriorating trends of these catalysts were well elucidated by the hydrophobicity of catalyst surface and the adsorption strength of water vapor.

A zeolite containing transition metal ions is usually paramagnetic and absorb the spectrum in the ultraviolet and visible regions. Accordingly, Kubelka-Munk function of the optical spectra may represent the surroundings of the copper ions on the surface of zeolite[9]. Water vapor was adsorbed on the catalysts for 30 min. at the temperatures ranging from room temperature to $450^\circ C$ and their optical spectra were recorded at room temperature. As shown in Fig. 3, a strong absorption band appeared at $12,500cm^{-1}$ which reflects the water coordinated on the copper ions in the zeolites. It well agrees with the results of copper complexes in homogeneous copper solution as a reference. As the adsorption temperature increases, the absorption band becomes weaker. For CuNZA catalyst, no band for H_2O adsorption can be found at $250^\circ C$ of adsorption temperature. Water coordinated on the copper ions strongly inhibits NO adsorption on the catalyst surface.

To elucidate competitive adsorption between NO and H_2O , they were individually or simultaneously adsorbed on each catalyst. As shown in Fig. 4, the desorption pattern of NO basically identical between the adsorption of NO alone and with H_2O , but the adsorption capacity of NO is dramatically decreased for the

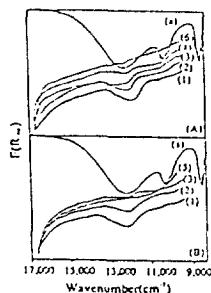


Fig. 3 Optical reflectance spectra of (A) CuHM and (B) CuNZA. (a) indicates the spectra of 0.5N $\text{Cu}(\text{NO}_3)_2$ solution. The spectra was recorded at room temperature with a sample adsorbed water at 25(1), 100(2), 250(3), 350(4), 400(5), and 450°C(6).

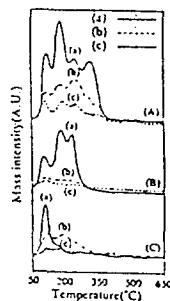


Fig. 4 TPD of the catalysts adsorbed NO only and NO with H_2O : (A) CuHM; (B) HM; (C) CuNZA (a) indicates the adsorption of NO; (b) the summation of nitrogen compounds formed by the simultaneous adsorption; (c) the simultaneous adsorption of NO and H_2O

simultaneous adsorption. The adsorption capacity of NO over HM catalyst is much less than that over CuHM catalyst. It confirms that HM catalyst is easily deactivated by H_2O as illustrated in Fig. 1. For CuNZA catalyst, the similar NO adsorption capacity was observed for the both adsorption of NO with and without H_2O by the summation of the nitrogen compounds, NO, NO_2 , N_2O and N_2 during TPD. It indicates that the adsorption capacity of NO for CuNZA catalyst is not altered by water vapor.

Based upon the present characterization of the catalysts, the inactivation of NO adsorption sites on the catalyst surface by water vapor is one of the crucial causes of the activity loss of NO reduction in wet condition. The degree of the change of NO adsorption capacity well illustrates the deactivation phenomenon of each catalyst by H_2O . It also agrees with the hydrophobicity of the catalysts employed in this study.

From the study of adsorption isotherms, the adsorption amounts of ethene on the catalyst surface is two times larger than propene. However, the heat of adsorption of propene is approximately 7.1 kcal/mol which is two times larger than ethene. Accordingly, propene probably exhibits stronger interaction with the catalyst surface than ethene. By the measurement of the amounts of reductant irreversibly adsorbed on the catalyst surface, it confirms that propene on the catalyst is mainly chemisorbed. Propene on CuNZA catalyst may be kept more stably than ethene on its adsorption site even under water containing condition. Thus, it may provide higher water tolerance of the catalytic system by propene.

For the effect of side reaction of hydrocarbons on NO reduction, the product distribution of this reaction system shown in Fig. 5 (A) and (B), mainly formic acid,

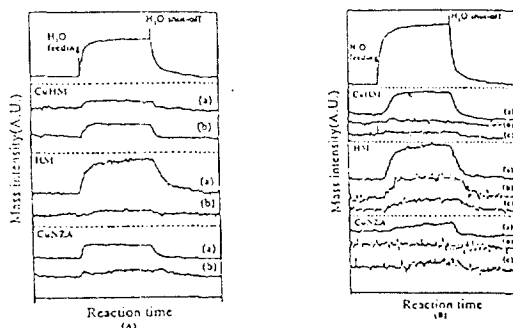


Fig. 5 Product distribution of NO reduction by hydrocarbons with H_2O : (a) Formic acid; (b) Formaldehyde; (c) Acrolein. Reaction condition: (A) NO 500ppm, C_2H_4 1,000ppm, O_2 4.2%, and $T=360^\circ\text{C}$; (B) NO 500ppm, C_3H_8 2,000ppm, O_2 4.2%, and $T=400^\circ\text{C}$.

formaldehyde and acrolein, is closely examined. When C_3H_6 is employed as a reductant, the formation of acrolein is observed along with formic acid and formaldehyde. It has already been reported that selective oxidation of C_2H_4 and C_3H_6 into formaldehyde and/or acrolein can occur over a zeolite catalyst containing transition metal ions[10]. These products are formed regardless of the feed of NO into the reaction system. It suggests that these side reactions may also be a cause of the activity deterioration of this catalytic system by H_2O .

CONCLUSION

The inhibition of NO adsorption sites by water vapor is one of the crucial reasons of the activity loss of NO reduction under water containing condition. It well agrees with the hydrophobicity of the catalysts. The side reaction of hydrocarbons producing formic acid, formaldehyde, and acrolein may play a role for the deactivation of the catalysts examined in this study. The adsorption characteristics of reductants on the catalyst surface is also important for the deactivation of mordenite type zeolite catalyst by water.

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