# CHAPTER VI
# THE IMPACT OF HYDRO-TREATMENT ON THE ACTIVITY OF 200%Cu/MFI AND H-Co-silicate FOR NITRIC OXIDE CONVERSION

## 6.1 Introduction

As mentioned in Chapter V, 200%Cu/MFI is an effective catalyst for NO conversion. However, a key issue in practical implementation of metal zeolite catalysts for nitric oxide removal is the capability and stability of catalyst in severe condition. The coexistence of water is one issue affected the activity of Cu/MFI [116]. This chapter concerns the effect of steam in the feed gas on the activity of 200%Cu/MFI. At first, the amount of steam (0-10 mol% $H_2O$) in the feed gas was studied on 200%Cu/MFI catalyst. Metallosilicate catalyst was also taken into account to compare the activity for NO removal with 200%Cu/MFI in both dry and wet condition. Since it is well known that metallosilicates have high resistance for steam and temperature as mentioned above by Inui et al.[95-102]. In this chapter, H-Co-silicate was also chosen to investigate since it was found by Inui et al. [103, 104] that H-Co-silicate provides high activity for NO conversion using n-octane as reductant in the excess oxygen atmosphere. Furthermore, 10 mol% $H_2O$ is practically presented in outlet gas of automobile and stationary sources [21]. Therefore, we also considered the amount of 10%$H_2O$ with temperature pretreatment conditions in the comparison of NO conversion of 200%Cu/MFI with H-Co-silicate.

## 6.2 Experimental

### 6.2.1 Catalyst preparation

Rapid crystallization method proposed by Inui [97] was applied to synthesize 200%Cu/MFI catalyst. The charged Si/Al atomic ratio was set at 50. As for H-Co-silicate catalyst, it was supported by Prof. Inui's laboratory. By ICP analysis, the Si/Al atomic ratio is around 257.

### 6.2.2 Reaction test

The catalytic reaction was carried out using an ordinary flow microreactor under atmospheric pressure. To reduce the pressure drop during the reaction test, the catalyst as powder form was tabletted, crushed, and sieved into 12 - 22 mesh. In order to investigate the activity for NO removal, catalyst was heated in a He stream from room temperature to 600°C and maintained at 600°C for 30 min. After that, a

feed gas composed of 1,000 ppm NO, 1,000 ppm n-octane, 2 mol% $O_2$, balanced with He was allowed to flow with a GHSV of 30,000 $h^{-1}$. As for wet condition, the amount of water vapor (0-10 mol% $H_2O$) was included in reaction feed gas. Every 10 min after introducing the feed gas to ensure the steady state of catalytic activity, the reactants and products were analyzed by gas chromatographs (Chrompack, Micro GC CP 2002 with MS-5A and porapak Q column) equipped with integrators. The reaction test was undertaken every 50°C diminishing from 600°C to 200°C followed the same procedure as mentioned above. The catalytic activity of nitric oxide reduction and n-octane combustion were investigated as the amount of $N_2$ and carbon oxides ($CO_x$; $CO_2$+CO) produced, respectively.

**6.3 Results and discussion**

6.3.1 The impact of the amount of steam on nitric oxide removal of 200%Cu/MFI

The effect of water vapor presence on NO conversion was analyzed on 200%Cu/MFI with various amount of water vapor (0-10mol% $H_2O$) in the feed gas. Figures 6.1 and 6.2 demonstrate NO and n-octane conversions of 200%Cu/MFI sequentially. It was shown that 200%Cu/MFI can exhibit high activities for both NO and n-octane conversions even the existence of 10 mol% $H_2O$ in the feed gas. It can be suggested that the existence of only steam in the feed gas has an infinitesimal effect on the activity of 200%Cu/MFI in nitric oxide conversion. The possible reason is that 200%Cu/MFI composes of a large amount of active species preserving high NO conversion. By investigating carefully, however, it can be identified that the larger amount of water vapor existed in the feed gas, the lower the activity for NO conversion of 200%Cu/MFI.

6.3.2 Comparative study for NO removal of 200%Cu/MFI and H-Co-silicate with and without 10mol% $H_2O$ in the feed gas

In order to compare the activity for NO removal in dry and wet conditions, conversions of NO and n-octane of 200%Cu/MFI and H-Co-silicate were investigated. Figures 6.3 and 6.4 demonstrate conversions of NO to $N_2$ and n-octane to $CO_x$ of 200%Cu/MFI and H-Co-silicate with and without the existence of 10 mol% $H_2O$. It was shown that 200%Cu/MFI exhibits higher activity for both conversions of NO and n-octane than H-Co-silicate. As demonstrated in Figures 6.3 and 6.4, it showed that H-Co-silicate relatively maintains the activity for NO removal. As for Cu/MFI, the activity for NO conversion does not change distinctively. However, there is a decreasing trend of NO conversion when Cu/MFI was carried out in wet

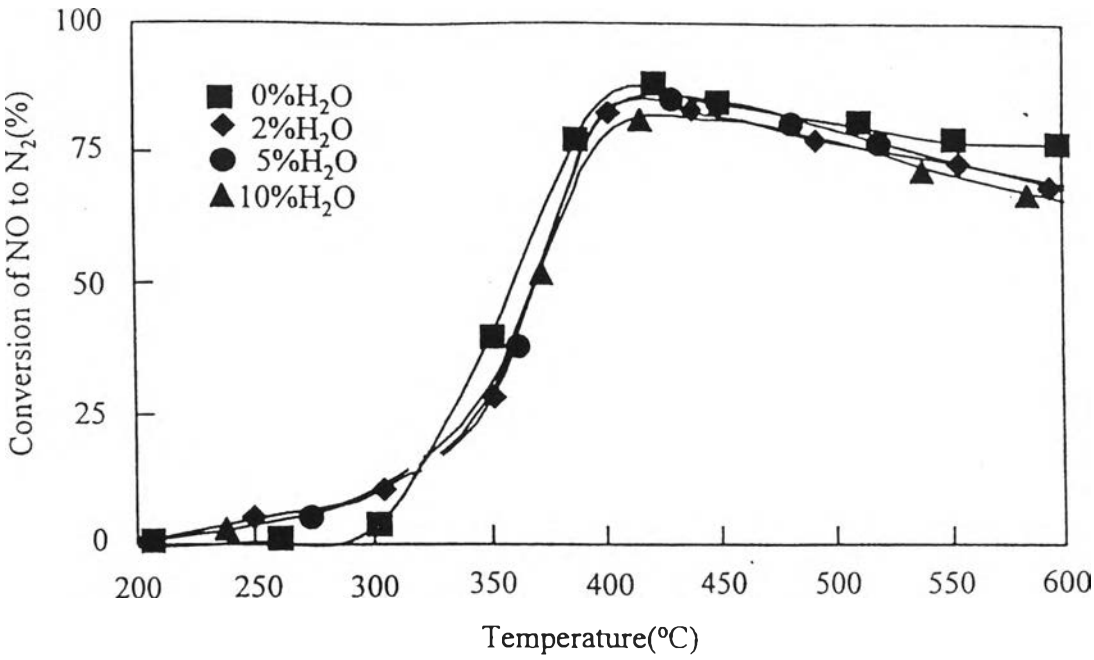


**Figure 6.1** The effect of $H_2O$ on the activity for NO conversion to $N_2$ of 200%Cu/MFI
Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, $O_2$ 2mol%, $H_2O$, He balance,
GHSV 30,000 $h^{-1}$

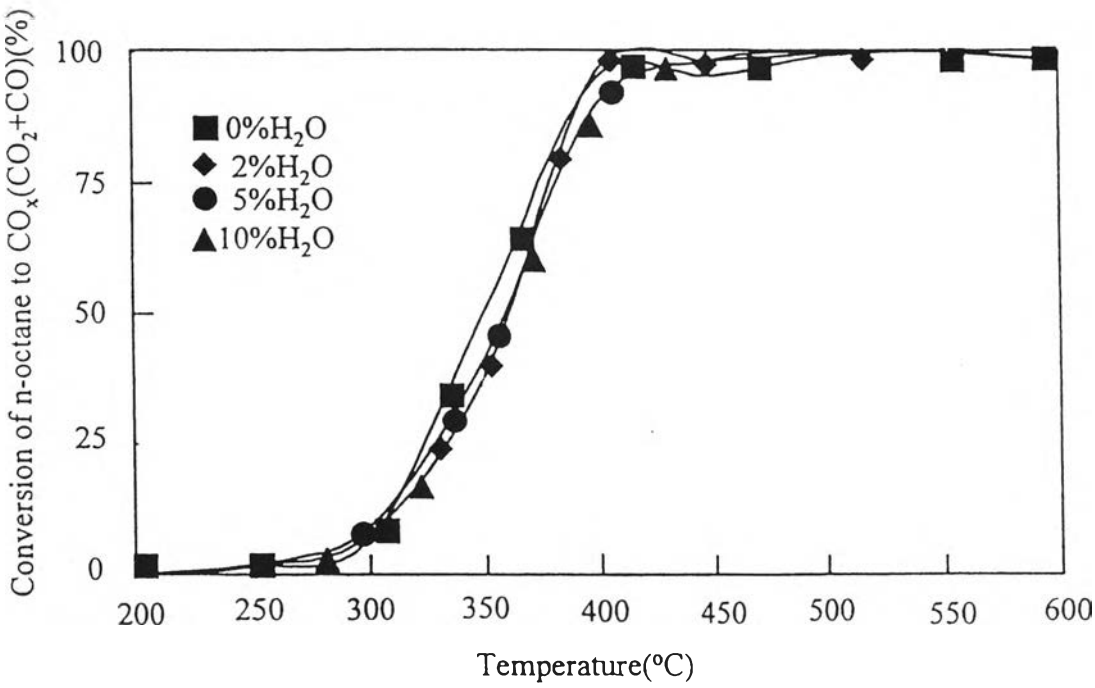


**Figure 6.2** The effect of $H_2O$ on the activity for n-octane conversion of 200%Cu/MFI
Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, $O_2$ 2mol%, $H_2O$, He balance,
GHSV 30,000 $h^{-1}$

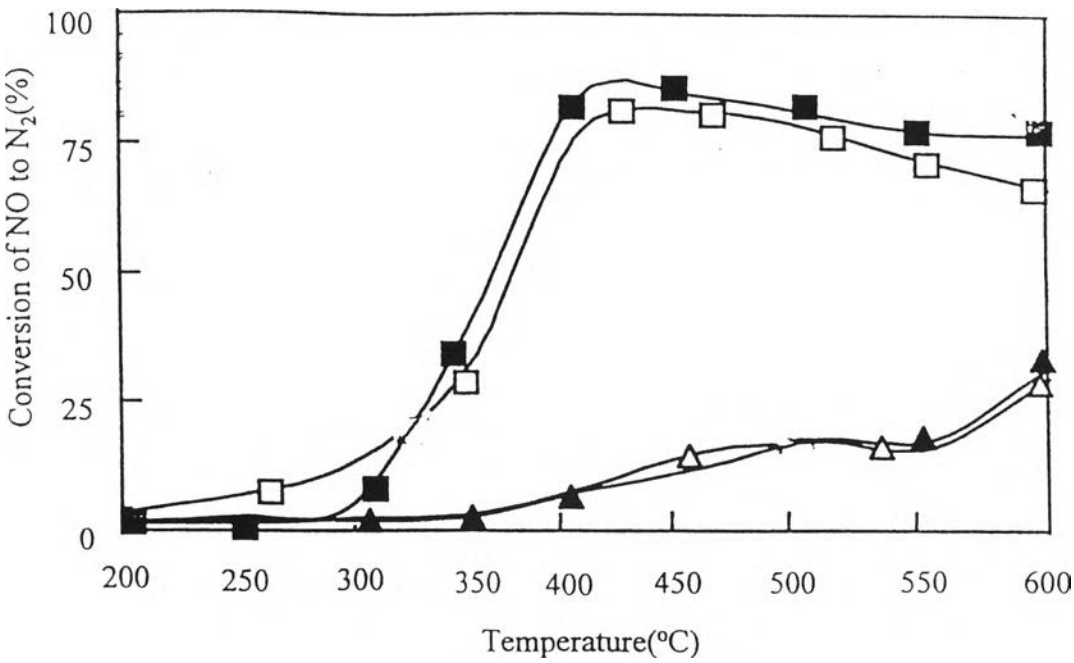


**Figure 6.3** The effect of 10mol% $H_2O$ in the feed gas on NO conversion of catalysts
Symbols: square symbol: 200%Cu/MFI, triangle symbol: H-Co-silicate; closed symbol: without 10mol% $H_2O$in the feed gas, opened symbol: with 10mol% $H_2O$ in the feed gas
Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, $O_2$ 2mol%, He balance, GHSV 30,000$h^{-1}$

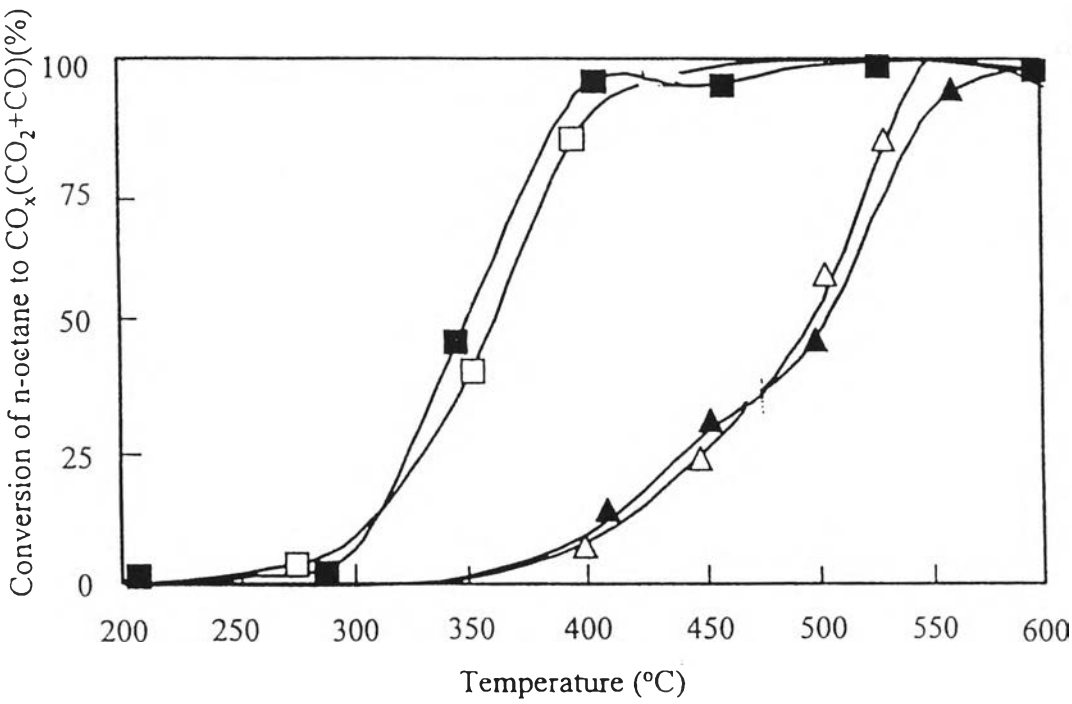


**Figure 6.4** The effect of 10mol% $H_2O$ in the feed gas on n-octane conversion of catalysts
Symbols: square symbol: 200%Cu/MFI, triangle symbol: H-Co-silicate; closed symbol: without 10mol% $H_2O$ in the feed gas, opened symbol: with 10mol% $H_2O$ in the feed gas
Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, $O_2$ 2mol%, He balance, GHSV 30,000$h^{-1}$

stream. The infinitesimal decrement of NO conversion of Cu/MFI in this study is possibly due to the large amount of active copper species on the catalyst preserving high activity for NO conversion even it was operated in wet condition. The deactivation of Cu/MFI by the presence of steam in the feed gas was also supported by Abreu et al. [74].

**6.4 Conclusion**

The coexistence of steam in the feed gas has an infinitesimal effect on conversions of NO and n-octane of both 200%Cu/MFI and H-Co-silicate catalysts. Due to the large amount of active copper sites on 200%Cu/MFI, the activity for nitric oxide removal was not decreased visibly. By comparing with conversion of nitric oxide in dry condition, however, H-Co-silicate can maintain the activity for nitric oxide removal in wet condition better than 200%Cu/MFI.