

THE EFFECT OF H₂O ON THE ACTIVITY OF
Cu/ZSM5-BASED CATALYSTS FOR LEAN-NO_x REDUCTION

Hung-Wen Jen, Cliff Montreuil, and Haren Gandhi
Chemical Engineering Department
Ford Research Laboratories, Ford Motor Company
Mail Drop 3179, 20000 Rotunda Drive
Dearborn, MI 48121

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INTRODUCTION

The reports on the high activity of Cu/ZSM5 catalysts for the reduction of NO in excess O₂ [1,2] have generated great interest in automotive industry. The successful development of catalysts capable of catalyzing the NO_x-reduction under lean conditions is a requisite for the application of lean-burn engine technology to production vehicles. The technology offers the potential of enhancing fuel economy and lowering engine-out pollutants [3]. A practical automotive catalyst has to have sufficient activity and long-term durability over the entire range of operating conditions.

In the process of evaluating Cu/ZSM5-based catalysts for lean-NO_x reduction in our laboratory, it was found that the activity decreased as the time on-stream increased. Later, the main cause of the deactivation was determined to be H₂O (steam). The deactivation has been shown to be accompanied by de-alumination of the zeolite structure using ²⁷Al-nmr spectroscopy [4]. The deactivation of Cu/ZSM5 under conditions of typical vehicle exhaust is well known now, but there is no report with detailed data representing the process of steam deactivation and comparing the reactivities of fresh and deactivated catalysts under a broad range of temperatures.

In this report, the results from our study concerning the effects of steam on the activities of Cu/ZSM5 catalysts are presented. The detailed data for the experiments leading to the finding of steam deactivation are included. Also, the activities for fresh and steam-deactivated Cu/ZSM5 catalysts are compared between 300 and 600 °C. The temporary effect of steam poisoning on the activities for lean-NO_x reduction depended on the catalysts. The variation may be related to the nature of Cu-sites on the Cu/ZSM5 catalysts.

EXPERIMENTAL

The catalysts used in this report were either powder samples or cordierite monoliths washcoated with Cu/ZSM5. Cu/ZSM5 materials were prepared by a conventional exchange method using HZSM5 or NaZSM5 and Cu-acetate. The activity of a catalyst in a flow reactor system was determined by the difference between the inlet and outlet concentrations of a reaction gas. Gas concentrations were monitored using commercial gas analyzers for NO_x, HC (total hydrocarbon), CO, and O₂.

RESULTS AND DISCUSSION

In Figure 1, the activity of a monolith catalyst containing Cu/ZSM5 was measured versus the time in the exhaust generated from a pulsed flame combustor [5]. In the combustor, isooctane vapor mixed in a flow of air was thermally combusted. Extra oxygen was added into the exhaust to simulate lean-burn engine exhaust. The NO_x-conversion decreased with the on-stream time. One hour on stream was comparable to 30 miles of vehicle operation. The durability of the Cu/ZSM5-based catalyst in the exhaust of combusted isooctane was not good.

There are several possible sources that can deactivate a catalyst in the automobile exhaust. The results in Figure 2 were obtained to determine the effect of SO₂. The NO_x-conversions for two identical monolith catalysts were measured. One catalyst was exposed to a synthetic gas mixture with 20 ppm SO₂, while the other one was exposed to the same gas mixture but without SO₂. The NO_x-conversion for either catalyst decreased with time. The

two curves of NO_x-conversion versus time were superimposable. The comparison in Figure 2 clearly shows that SO₂ is not the cause of the observed deactivation.

Figure 3 shows the activities of three identical catalysts versus aging time. The aging process was simply the heating of a catalyst in a flow of air. After a certain period of aging, the catalyst was moved to a flow reactor system and the activity was measured using a dry mixture of reaction gases. Two catalysts were aged at 480 °C, one in dry air and the other in wet air containing 10% H₂O. The conversion of NO_x, HC or CO remained constant for 300 hours over the catalyst aged in dry air. The conversion for the catalyst aged in wet air at 480 °C decreased with aging time. The sole difference between the constant and decreasing activities was the existence of 10% H₂O in the aging media (air). Clearly, the heating in the presence of H₂O-steam caused the deactivation of Cu/ZSM5 catalysts. The decrease in the activity for the catalyst aged at 380 °C in wet air was also detectable, even though the rate of decrease was smaller than that aged at 480 °C.

In order to compare the activities in a broad range of temperatures, the NO_x-conversion for a fresh CuNaZSM5 catalyst was measured in a temperature-programmed-cooling process from 600 to 300 °C at 12 °C/min (Figure 4). The addition of 9% H₂O into the reaction mixture caused a significant decrease in the NO_x-conversion. The activity generally could be regained when the 9% H₂O was turned off, if the exposure to the steam was not long and the temperature was not very high. The same experiment was done for the same catalyst which had been aged in 20% H₂O (figure 5). The NO_x-conversion for the aged catalyst was lower than that for the fresh catalyst as expected. However, the addition of 9% H₂O had little effect on the NO_x-conversion of the aged catalyst. The result indicated that the part of the activity vulnerable to the temporary poisoning of the steam present in the reaction mixture was the first lost to the long term steam-deactivation. The phenomenon may be related to the existence of different Cu-sites on Cu/ZSM5 catalysts.

CONCLUSION

Cu/ZSM5-based catalysts for lean-NO_x reduction deactivated after long term exposure to the simulated exhaust gas mixture. The cause of deactivation is the exposure at high temperature to steam that is always present in vehicle exhaust. For the fresh CuNaZSM5 catalyst, H₂O had a temporary poisoning effect on the NO_x conversion. For the steam-aged CuNaZSM5 catalyst, the poisoning effect of H₂O on the NO_x-conversion was not noticeable.

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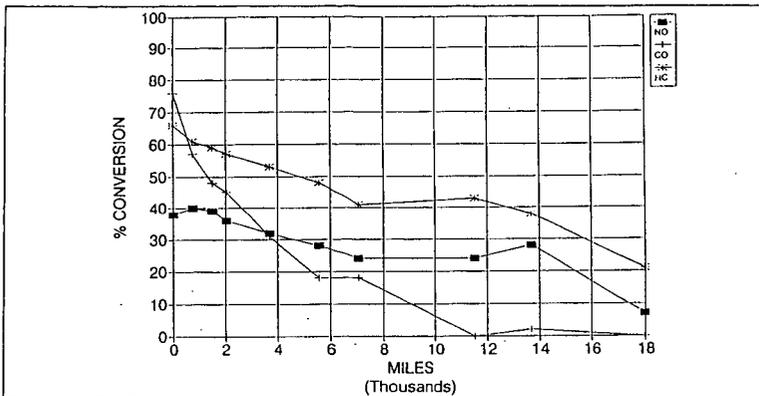


Figure 1. Activity of Cu/ZSM5-Containing Monolith aged in Pusted Flame Combustor
 $\text{SiO}_2/\text{Al}_2\text{O}_3=32$, 2.41wt% Cu on Cu/ZSM5, $\text{SV}=30,000 \text{ hr}^{-1}$, $T=482 \text{ }^\circ\text{C}$

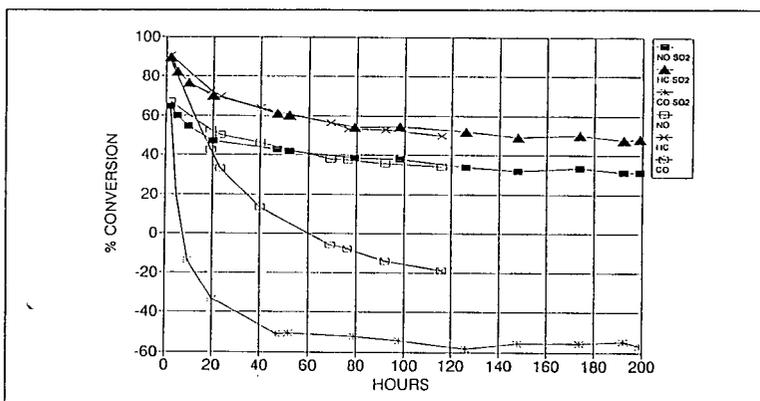


Figure 2. Effect of Aging in SO_2 for Cu/ZSM5-containing Monolith in Flow Reactor
 $\text{SiO}_2/\text{Al}_2\text{O}_3 = 32$, 2.41wt% Cu on Cu/ZSM5, $\text{SV} = 50,000 \text{ hr}^{-1}$, $T = 482 \text{ }^\circ\text{C}$
 3.45% O_2 , 1517 ppm C_3H_6 , 756 ppm C_3H_8 , 490 ppm NO, 0.3% CO, 0.1% H_2 ,
 12% CO_2 , 10% H_2O , N_2 balance

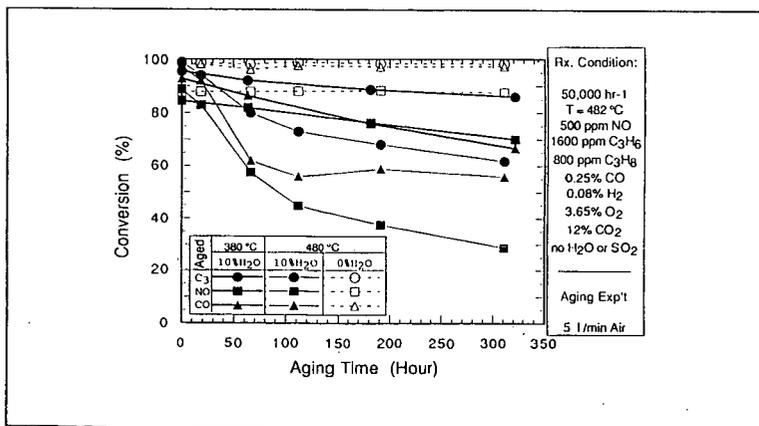


Figure 3. Effect of Aging in H_2O for Cu/ZSM5-containing Monolith in Flow Reactor
 $\text{SiO}_2/\text{Al}_2\text{O}_3 = 32$, 2.41wt% Cu on Cu/ZSM5

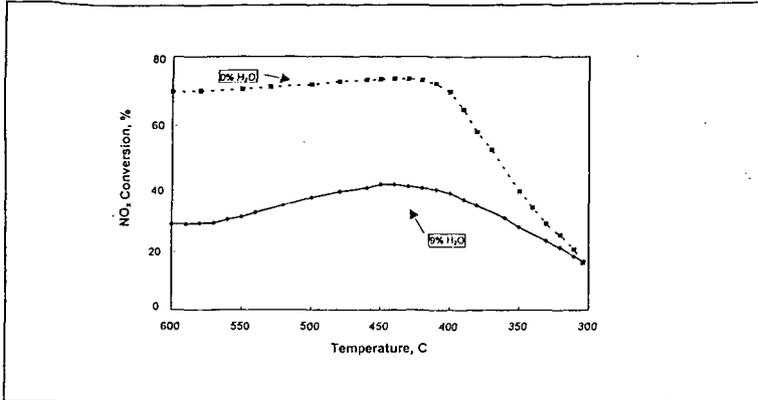


Figure 4. Effect of H₂O in Reaction Mixture on NO-conversion for Fresh CuNaZSM5
 $\text{SiO}_2/\text{Al}_2\text{O}_3 = 46$, 2.8 wt% Cu, 0.15 g sample
 5% O₂, 1120 ppm C3 ($\text{C}_3\text{H}_6/\text{C}_3\text{H}_8 = 2$), 550ppm NO, 0.5 l/min Flow

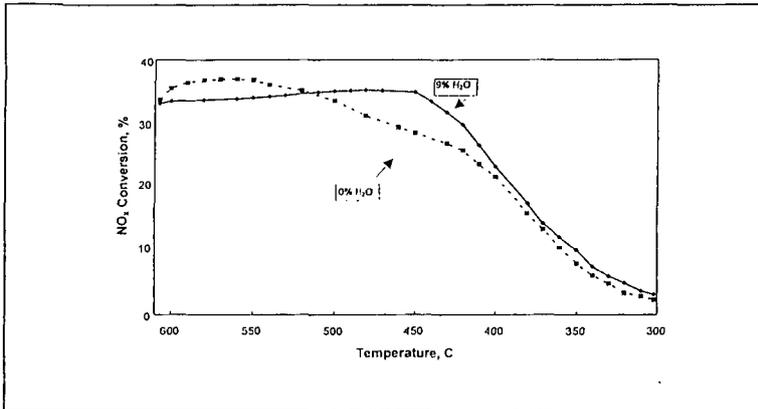


Figure 5. Effect of H₂O in Reaction Mixture on NO-conversion for Steam-aged CuNaZSM5
 $\text{SiO}_2/\text{Al}_2\text{O}_3 = 46$, 2.8 wt% Cu, 0.15 g sample
 5% O₂, 1120 ppm C3 ($\text{C}_3\text{H}_6/\text{C}_3\text{H}_8 = 2$), 550ppm NO, 0.5 l/min Flow