Effect of Pt dispersion on the reduction of NO by propene over alumina-supported Pt catalysts under lean-burn conditions

Jong-Hwan Lee and Harold H. Kung [*]

Center for Catalysis and Surface Science, Northwestern University, Evanston, IL 60208, USA

Received 15 October 1997; accepted 12 January 1998

Reduction of NO by propene under lean-burn exhaust conditions and oxidation of NO were studied on two Pt/γ-Al_2O_3 catalysts of 4.4% and 82% dispersion of Pt. At 265 °C, the turnover frequency for the oxidation of NO was over 100 times higher on the low dispersion than the high dispersion catalyst. The difference was much less pronounced for the reduction of NO. In the reduction of NO, the N_2O/N_2 ratio in the product was found to increase with the conversion of hydrocarbon, while depend much less on Pt dispersion, temperature, or NO conversion.

Keywords: Pt dispersion effect, NO reduction, propene reduction of NO, NO oxidation, NO_2 reduction

1. Introduction

The selective reduction of NO with hydrocarbons in the presence of excess oxygen has been studied extensively over the years as a promising method to remove NO from stationary and mobile sources. Although a number of zeolite, metal oxide, and noble metal catalytic systems have been reported to show relatively high catalytic activity for this reaction [1–3], few have been found to satisfy all the requirements for commercial application. Since Pt is the most effective catalyst at low temperatures [4] and resistant toward activity suppression by water [5] and sulfur [6], it appears to be important to understand this catalytic system.

The use of Pt for exhaust gas treatment has been studied extensively for two decades because Pt is a major component in the current automobile exhaust (or three-way) catalysts. However, its catalytic behavior under the exhaust condition of lean-burn gasoline engines has not been studied in detail until recently [7–15]. In laboratory tests, up to about 60% conversion of NO could be achieved. However, substantial amounts of N_2O are formed as a product [16]. It has been reported that the selectivity for N_2 or N_2O depends on the temperature and/or NO conversion [16], and the activity differs depending on whether SiO_2 or Al_2O_3 is used as support [17] and the nature of the hydrocarbon reductant [14]. There is evidence that the reaction mechanism involves the reaction between adsorbed NO and a surface hydrocarbon species [12,13], instead of, or in addition to NO decomposition and reduction of the oxidized catalyst by hydrocarbon [10]. There is also indication that the NO reduction activity depends on the Pt dispersion; the turnover frequency (TOF) is higher for lower Pt dispersion [16]. This latter finding of the effect of dispersion is similar to that reported for the reduction of NO by H_2 [18] and the oxidation of propane [19]. Interestingly, the effect of dispersion on CO oxidation varies, depending on the reaction condition ([20] and references therein). Structure sensitivity is also observed in NO reduction by CO on Pd [21] and Rh [22] catalysts.

The purpose of this study is to investigate further the effect of Pt dispersion. In addition to comparing the NO reduction activity, the selectivity for N_2 and N_2O, and the activity for NO oxidation to NO_2 are also compared on two Pt/Al_2O_3 catalysts of different dispersions. The results of this investigation are reported here.

2. Experimental

Two Pt samples of different Pt dispersions were prepared by the incipient wetness technique using $Pt(NH_3)_2(NO_2)_2$ dissolved in dilute NH_4OH. The solution was added to 60–80 mesh γ-alumina (American Cyanamid, BET surface area: 126 m^2/g, pore volume: 0.49 cm^3/g), which was then dried at 100 °C in air for 40 h. The low Pt dispersion sample was calcined at 400 °C for 3.5 h and reduced in H_2 at 500 °C for 18 h, whereas the high dispersion sample was calcined at 400 °C for 1 h and reduced at 500 °C for 6.5 h. The metal dispersions, as measured by H_2 chemisorption at 298 K using H_2 pulses, were 4.4% and 82%. The metal loading was 0.30% for the low dispersion and 0.27% for the high dispersion sample.

For NO reduction, a 200 ml/min flow of 930 ppm NO, 930 ppm C_3H_6, 5% O_2, 1.6% H_2O and balance He was passed over a catalyst. Typically, 0.1–0.3 g of the low dispersion catalyst and 0.05–0.15 g of the high dispersion catalyst were used. For NO oxidation, the same feed mixture but without propene or water was used with 0.1 g catalyst at the same total flow rate. For NO_2 reduction, the same feed except with 900 ppm NO_2 and 80 ppm NO instead of

---

[*] To whom correspondence should be addressed.

Table 1
Reduction of NO and propene oxidation over 0.1 g low dispersion Pt/Al_2O_3 catalyst.

Temp.	NO reduction					C_3H_6 oxidation
(°C)	% yield to N_2	% yield to N_2O	% yield to NO_2	% NO conv.	% C_3H_6 conv.	% C_3H_6 conv.
265	13.1	3.6	2.6	19.3	26.4	100
275	19.2	14.3	3.5	37.0	74.6	100
285	20.5	18.6	4.0	42.9	100	100
300	16.4	15.9	18.7	51.0	100	100

Table 2
Reduction of NO and propene oxidation over 0.1 g high dispersion Pt/Al_2O_3 catalyst.

Temp.	NO reduction					C_3H_6 oxidation
(°C)	% yield to N_2	% yield to N_2O	% yield to NO_2	% NO conv.	% C_3H_6 conv.	% C_3H_6 conv.
255	12.6	6.9	2.6	22.1	34.3	100
265	18.3	21.4	4.5	44.2	100	100
275	16.8	20.7	5.8	43.3	100	100
285	10.1	18.9	7.0	36.0	100	100

Table 3
NO oxidation over 0.1 g Pt/Al_2O_3 catalysts.

Temp.	% NO conversion	
(°C)	Low Pt dispersion	High Pt dispersion
255		2.1
265	39	4.6
275	47	5.3
285	51	7.5
300	57	

NO was used with 0.1 g catalyst at the same total flow rate. The reaction products were monitored with a gas chromatograph using a Porapak Q and a molecular sieve 5A column and NO_x chemiluminescence analyzer.

3. Results and discussion

Tables 1 and 2 show some sample data for the reduction of NO over the two catalysts. From these data, it can be seen that the activities for the two catalysts were similar, with the low dispersion catalyst being somewhat more active. At 245 °C, the TOF for NO conversion was estimated to be 10 min^{-1} for the low dispersion sample, and 0.8 min^{-1} for the high dispersion sample, using data at 30–40% conversion of propene and about 20% conversion of NO. These values were approximate because they were not obtained under differential conditions. Although similar maximum total NO conversions were achieved by the two catalysts, more N_2O was produced than N_2 over the high dispersion sample when the propene conversion was close to 100%, whereas the N_2 yield was always higher than the N_2O yield on the low dispersion sample. This observation differed from the previous report [23], in which metal dispersion did not affect the selectivity toward N_2O.

On the other hand, the rates of NO oxidation were vastly different over the two catalysts, as shown in table 3, which agrees with the literature report [9]. At 265 °C, the TOF of the low dispersion sample was >50 min^{-1}, compared with 0.3 min^{-1} for the high dispersion sample, estimated using relatively high conversion data for the former catalyst. However, although the activity for NO oxidation was much higher for the low dispersion sample, only small amounts of NO_2 were present in the exit gas during NO reduction. Thus, either the presence of hydrocarbon reductant suppresses the NO oxidation activity, or the NO_2 formed is rapidly reduced back to NO. For the high dispersion sample, only small amounts of NO_2 were observed in the exit gas, also consistent with its low activity for NO oxidation.

Reduction of NO_2 by propene was studied, and the results are summarized in table 4. On both catalysts, reduction of NO_2 to NO was very fast, much faster than its reduction to N_2. This is consistent with the observed low NO_2 concentration in the gas phase during NO reduction. It also implies that NO reduction does not involve first formation of NO_2 followed by its reduction. Interestingly, similar N_2/N_2O ratios were observed as in NO reduction. This suggests that most likely, the reduction of NO_2 proceeds by its reduction to NO first, which is then reduced to N_2 or N_2O. Another interesting observation is that the rate of propene conversion was lower than during NO reduction. Probably, NO_2 suppresses the adsorption of O_2 and reduces the rate of propene oxidation. When all the propene is consumed, NO_2 appears in the gas phase again.

The effect of space velocity was studied by varying the amount of catalyst. As expected, using a larger sample lowered the temperature to achieve a certain NO conversion. When the N_2 and N_2O yields were plotted against propene conversion as shown in figures 1 and 2, a trend is observed that the selectivity for N_2O appears to be related primarily to the propene conversion, with smaller effect due to temperature, NO conversion, or Pt dispersion. The selectivity for N_2O increases with propene conversion. This dependence of N_2O selectivity on propene conversion dif-

Table 4
Reduction of NO_2 over 0.1 g Pt/Al_2O_3 catalysts.

Temp. (°C)	Low Pt dispersion				High Pt dispersion			
	% NO_2 to N_2	% NO_2 to N_2O	% NO_2 to NO	% C_3H_6 conv.	% NO_2 to N_2	% NO_2 to N_2O	% NO_2 to NO	% C_3H_6 conv.
265					7.2	3.2	94.5	31.1
275	6.2	2.0	94.8	30.5	12.0	15.9	74.6	92.2
285	14.9	15.2	73.8	92.3	14.3	16.4	71.5	100
300	16.8	15.4	43.1	100				

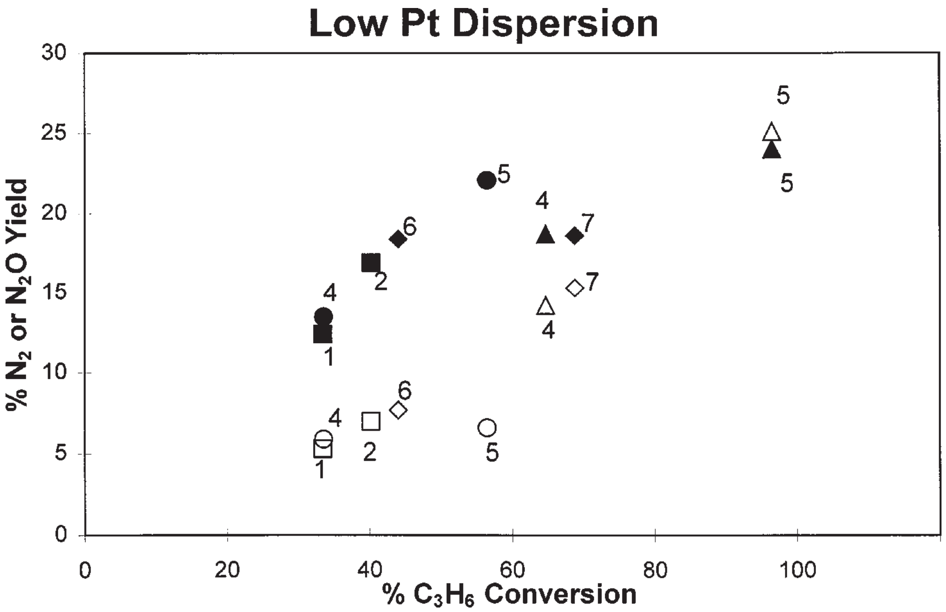

Figure 1. Relationship between propene conversion and yield of N_2 and N_2O over the low Pt dispersion sample obtained at various space velocities. Catalyst weight: 0.1 g (◆), 0.2 g (●), 0.25 g (▲) and 0.3 g (■). Closed symbols for N_2 and open symbols for N_2O. Temperatures in °C are: 240 (1), 245 (2), 250 (3), 255 (4), 265 (5), 275 (6) and 280 (7).

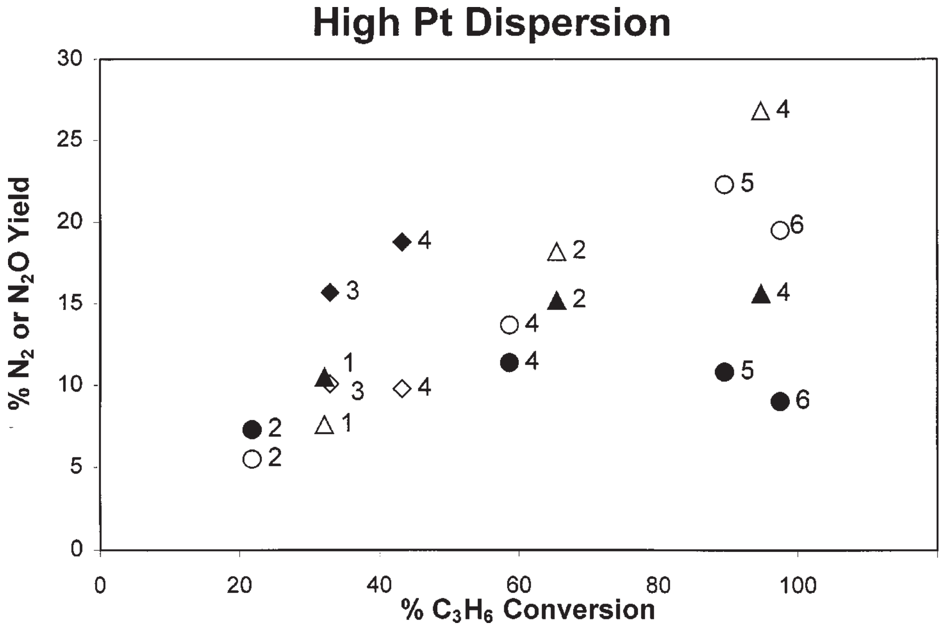

Figure 2. Relationship between propene conversion and yield of N_2 and N_2O over the high Pt dispersion sample obtained at various space velocities. Catalyst weight: 0.1 g (◆), 0.05 g (●) and 0.15 g (▲). Closed symbols for N_2 and open symbols for N_2O. Temperatures in °C are: 245 (1), 255 (2), 260 (3), 265 (4), 275 (5) and 285 (6).

fers from the literature result where no dependence was observed [13,18].

The increase in N_2O selectivity with increasing hydrocarbon conversion agrees with the mechanism of its formation. In the current understanding, N_2O is formed from molecular adsorption of NO, which is preferred to dissociative adsorption when the density of free surface Pt atoms is low. At low hydrocarbon conversions, the partial pressure of hydrocarbon is high (relatively), correspondingly the surface is covered with a high density of hydrocarbon intermediates, which react with NO to form N_2 [15]. As the hydrocarbon conversion increases, the density of such intermediates decreases, while the fraction of free Pt and oxygen-covered surface increases, which favors the formation of N_2O [11,14].

It is interesting that the rate of oxidation of NO depends much more strongly on Pt dispersion than NO reduction. The reduction of NO has been proposed to involve a cluster of five or more Pt atoms [18]. Thus, one would expect this process to depend quite strongly on the Pt dispersion. The relatively small effect of Pt dispersion could be due to the fact that the predominant reaction is between adsorbed NO and the surface hydrocarbon species, which would require as little as only adjacent Pt atoms. On the other hand, one would expect the NO oxidation reaction to be similar to CO oxidation. CO oxidation has been shown to occur much faster on a more highly dispersed Pt catalyst at low pressures [20], but the dispersion dependence decreases at high pressures. In the low pressure regime, the kinetics is strongly influenced by the rate of desorption of CO, which is a structure-sensitive process. Perhaps the rate of desorption of NO is also structure-sensitive, and the strong effect of Pt dispersion on NO oxidation is observed at the low pressures of NO used here.

In conclusion, the dependence on Pt dispersion of NO oxidation and propene reduction of NO was studied. The turnover rate of NO oxidation to NO_2 depends strongly on the Pt dispersion. The dependence is much weaker for the reduction of NO. Thus, the reduction of NO does not involve NO oxidation to NO_2. In the reduction of NO, the N_2O/N_2 ratio in the product depends much more strongly on the conversion of hydrocarbon than Pt dispersion, temperature, or NO conversion. The latter result can be explained by the mechanism that the formation of N_2O is favored on an oxygen-covered surface, and N_2 is formed on a surface covered with hydrocarbon intermediates.

Acknowledgement

This work was supported by the US Department of Energy, Basic Energy Sciences, and GM Corporation. The authors would like to thank Professor J. Butt for the supply of platinum catalysts.

References

[1] M.D. Amiridis, T. Zhang and R.J. Farrauto, Appl. Catal. B 10 (1996) 203.
[2] M. Iwamoto, Catal. Today 22(1) (1995).
[3] R. Burch, Catal. Today 26(2) (1996).
[4] R. Burch and P.J. Millington, Catal. Today 29 (1996) 37.
[5] A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno and H. Ohuchi, Appl. Catal. B 2 (1993) 71.
[6] G. Zhang, T. Yamaguchi, H. Kawakami and T. Suzuki, Appl. Catal. B 1 (1992) L15.
[7] R. Burch and S. Scire, Appl. Catal. B 3 (1994) 295.
[8] R. Burch and T.C. Watling, Appl. Catal. B 11 (1997) 207.
[9] E. Xue, K. Seshan and J.R.H. Ross, Appl. Catal. B 11 (1996) 65.
[10] R. Burch, P.J. Millington and A.P. Walker, Appl. Catal. B 4 (1994) 65.
[11] C. Rottländer, A. Andorf, C. Plog, B. Krutzsch and M. Baerns, Appl. Catal. B 11 (1996) 49.
[12] C. Rottländer, A. Andorf, C. Plog, B. Krutzsch and M. Baerns, J. Catal. 169 (1997) 400.
[13] R. Burch and T.C. Watling, Catal. Lett. 37 (1996) 51.
[14] R. Burch and T.C. Watling, Catal. Lett. 43 (1996) 19.
[15] S. Lacombe, J.H.B.J. Hoebink and G.B. Marin, Appl. Catal. B 12 (1997) 207.
[16] R. Burch and P.J. Millington, Catal. Today 26 (1995) 185.
[17] M. Inaba, Y. Kintaichi and H. Hamada, Catal. Lett. 36 (1996) 223.
[18] K. Otto and H.C. Yao, J. Catal. 66 (1980) 229.
[19] K. Otto, J.M. Andino and C.L. Parks, J. Catal. 131 (1991) 243.
[20] G.S. Zafiris and R.J. Gorte, J. Catal. 140 (1993) 418.
[21] S.M. Vesecky, P. Chen, X. Xu and D.W. Goodman, J. Vac. Sci. Technol. A 13 (1995) 1539.
[22] C.H.F. Peden, D.W. Goodman, D.S. Blair, P.J. Berlowitz, G.B. Fisher and S.H. Oh, J. Phys. Chem. 92 (1988) 1563.
[23] M.C. Demicheli, L.C. Hoang, J.C. Menezo, J. Babier and M. Pinabiau-Carlier, Appl. Catal. A 97 (1993) L11.