Catalysis Letters Vol. 100, Nos. 3–4, April 2005 (© 2005)
DOI: 10.1007/s10562-004-3462-5

Low-temperature SCR of NO with NH_3 over noble metal promoted Fe-ZSM-5 catalysts

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Received 7 October 2004; accepted 4 December 2004

We have reported previously the excellent performance of Fe-exchanged ZSM-5 for selective catalytic reduction (SCR) of NO with ammonia at high temperatures (300–400 °C). In this work, we found that the reaction temperature could be decreased to 200–300 °C when a small amount of noble metal (Pt, Rh, or Pd) was added to the Fe-ZSM-5. The SCR activity follows the order Pt/Fe-ZSM-5 > Rh/Fe-ZSM-5 > Pd/Fe-ZSM-5 at 250 °C. On the Pt promoted Fe-ZSM-5, 90% NO conversion was obtained at 250 °C at GHSV $= 1.1 \times 10^5\ h^{-1}$. Moreover, the noble metal improved the resistance to H_2O and SO_2. The presence of H_2O and SO_2 decreased the SCR performance only very slightly.

KEY WORDS: low-temperature SCR; Fe-ZSM-5; noble metal promoted Fe-ZSM-5; SCR; ammonia-SCR.

1. Introduction

Nitrogen oxides (NO, NO_2 and N_2O) remain a major source for air pollution. They contribute to photochemical smog, acid rain, ozone depletion and greenhouse effects [1]. Nearly all NO_x (95%) derives from transportation (49%) and power plants (46%) [2]. In recent years, many methods have been used to reduce the emission of nitrogen oxide. Catalytic technologies are attractive because of their low cost and high efficiency [1]. In the case of automotive catalytic converters, CO acts as the main reducing agent for NO [3,4]. Hydrocarbons such as methane, propane or propylene can also be used as reductants [5–9]. However, highly active and stable catalysts have not been found for hydrocarbon selective catalytic reduction (SCR).

The major technology for reducing nitrogen oxide emissions from stationary sources is SCR of NO_x ($x = 1, 2$) by ammonia. The general reaction is as follows:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

Many catalysts have been reported to be active for the above reaction [1]. The commercial catalysts for this process are V_2O_5/TiO_2 (anatase) mixed with WO_3 or MoO_3 [10–17]. Although the vanadium based catalyst are highly active and resistant to SO_2, there are also some disadvantages. This catalyst is active within a narrow temperature window of 300–400 °C, while this temperature range also helps to avoid pore plugging from the deposition of ammonium sulfate salts such as NH_4HSO_4 and $(NH_4)_2S_2O_7$ on the catalysts surface. Consequently, it is necessary to locate the SCR unit upstream of the de-sulfurizer and electrostatic precipitator in order to avoid reheating of the flue gas as well as deposition of dust on the catalyst [1]. The formation of N_2O is another drawback for the vanadium based catalysts [1].

Some transition metal containing catalysts have been investigated for the low temperature SCR reaction, such as chronaia [2], $NiSO_4/Al_2O_3$ [18], MnO_x/Al_2O_3 [19], V_2O_5/activated carbon [20], iron–silica aerogels [21], MnO_x/NaY [22], $MnOx/TiO_2$ [23] and other oxides [24]. They showed various SCR activities at below 200 °C under different conditions. Recently, we found that Fe–Mn, Ce–Mn, Ce–Mn/USY and Fe–Mn/TiO_2 based transition metal oxides [25–30] were highly active for low-temperature SCR of NO with NH_3 with 100% selectivity to N_2 at a high space velocity. Much work have been focused on zeolite-based catalysts for medium temperature SCR of NO with ammonia, but few studies have been done for the low-temperature SCR of NO with ammonia with zeolite-based catalysts. We have reported previously the excellent performance of Fe-exchanged ZSM-5 for SCR of NO with ammonia at high temperatures [31]. Recently, based on field test results [32], we found that Fe-ZSM-5 was significantly poisoned by mercury. In this paper, we found the reaction temperature can be decreased to 150–250 °C when a small amount of noble metal (0.1 wt% of Pt, Rh, or Pd) is added to the Fe-ZSM-5. Such a catalyst would be placed downstream the desulfurizer and electrostatic precipitator. Success in developing such a catalyst would significantly improve the economics of SCR. Moreover,

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there is still residual SO_2 remaining after the desulfurizer. Thus, SO_2 resistance needs to be considered.

2. Experimental

2.1. Preparation of catalysts

Fe-ZSM-5 was prepared by conventional ion-exchange procedure. About 2 g of NH_4-ZSM-5 (Si/Al = 10, from Alsi-Penta Zeolite Gmbh (Germany)) was added to 200 mL of 0.05 M $FeCl_2$ solution with constant stirring. After 24 h, the mixture was filtered and washed with large quantity of de-ionized water to remove chloride ions. The obtained sample was dried at 120 °C in air for 12 h and then calcined at 500 °C for 6 h in air. The noble metal (Pt, Pd and Rh) doped Fe-ZSM-5 catalysts were prepared by the incipient-wetness impregnation technique. The doped Fe-ZSM-5 sample was first dried at 120 °C overnight in air and then calcined at 500 °C for 4 h in air. The content of noble metal was controlled at 0.1% by weight (For molar percent, 0.0575% Pd, 0.0312% Pt and 0.0597% Rh). The Fe-ZSM-5 and noble promoted Fe-ZSM-5 catalysts were pressed into pellets and ground to 60–100 mesh before catalytic activity test.

2.2. SCR performance

The SCR activity measurements were carried out in a fixed-bed quartz reactor. The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm. NH_3, 2% O_2, and balance He. Under typical conditions, 200 mg sample was used in each run. The total flow rate was 500 ml/min (under ambient conditions). The premixed gases (1.01% NO in He, 1.00% NH_3 in He, and 0.99% SO_2 in He) were supplied by Matheson. Water vapor was generated by passing He through a heated gas-wash bottle containing de-ionized water. The tubing of the reactor system was heat traced to prevent formation and deposition of ammonium sulfate/bisulfate, and ammonium nitrate. The NO and NO_2 concentrations were continually monitored by a chemiluminescent NO/NO_x analyzer (Thermo Environmental Instruments Inc. Model 42C). To avoid errors caused by the oxidation of ammonia in the converter of the NO/NO_x analyzer, an ammonia trap containing phosphoric acid solution was installed before the sample inlet to the chemiluminescent analyzer. The products were also analyzed by a gas chromatograph (Shirmadzu, 8A) at 50 °C with 5A molecular sieve column for N_2 and Porapak Q column for N_2O.

3. Results and discussion

SCR of NO with ammonia was studied on various Fe-ZSM-5 based catalysts. Figure 1 shows the NO conversion on the Fe-ZSM-5 catalyst and that promoted by various noble metals. As expected, Fe-ZSM-5 catalyst showed high activities for SCR reaction at higher temperatures and relatively lower activities at lower temperatures. The NO conversion increased with increasing temperature and reached nearly 90% at 250 °C under the condition of GHSV $= 1.1 \times 10^5\ h^{-1}$, [NO] = [$NH_3$] = 1000 ppm. In the entire temperature range studied here, no N_2O was observed. When 0.1 wt% of Pt, Rh and Pd was doped on the Fe-ZSM-5, the activity for SCR of NO increased significantly (figure 1). At 250 °C, NO conversion increased in the following order: Fe-ZSM-5 < Pd/Fe-ZSM-5 < Rh/Fe-ZSM-5 < Pt/Fe-ZSM-5. It is clear that the addition of noble metal could be used to decrease the reaction temperature for NO conversion.

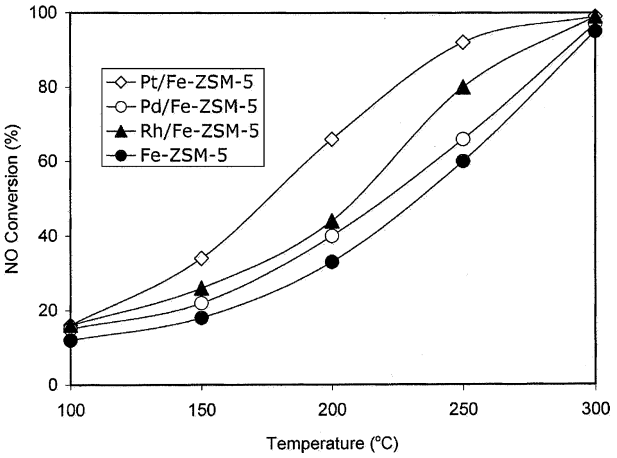

Figure 1. NO conversion on 0.1 wt% Pt, Pd and Rh doped Fe-ZSM-5 catalysts. Reaction conditions: 0.2 g catalyst, [NH_3] = [NO] = 1000 ppm, [O_2] = 2%, He = balance, total flow rate = 500 mL/min.

Figure 2 shows the N_2 selectivity of different Fe-ZSM-5 catalysts. It can be seen that the N_2 selectivity decreased with increasing temperatures. It is clear that

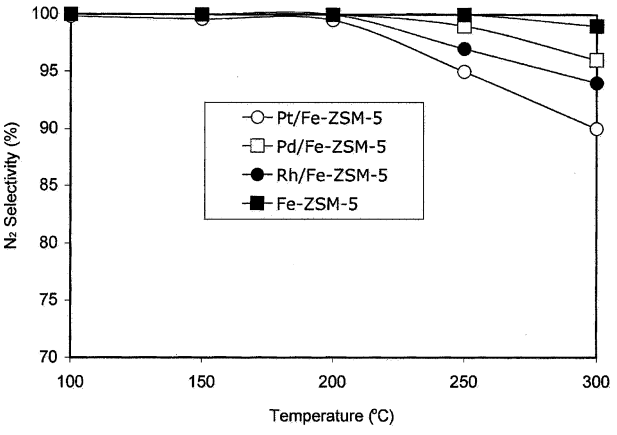

Figure 2. N_2 selectivity on 0.1 wt% Pt, Pd and Rh doped Fe-ZSM-5 catalysts. Reaction conditions: 0.2 g catalyst, [NH_3] = [NO] = 1000 ppm, [O_2] = 2%, He = balance, total flow rate = 500 mL/min.

the addition of noble metal decreased the N_2 selectivity. The N_2 selectivity decreased in the following order at 250 °C: Pt/Fe-ZSM-5 < Rh/Fe-ZSM-5 < Pd/Fe-ZSM-5 < Fe-ZSM-5. It is not surprising that the addition of noble metal could increase the activity for the SCR reaction. Xue *et al.* [33] reported that Pt-based catalysts are highly active for the oxidation of NO. For Fe-ZSM-5, Long and Yang [34] have shown that the oxidation of NO to NO_2 is the slow step in the ammonia SCR reaction. The addition of noble metal would increase the NO oxidation to NO_2, which would in turn increase the SCR activity on the Fe-ZSM-5 catalyst. This result is consistent with the report of Long and Yang [34] and that of Eng and Bartholomew [35]. During the SCR reaction, gaseous NH_3 molecules are adsorbed quickly onto the Brönsted acid sites to form ions, and NO molecules are oxidized to NO_2 by O_2. Then one molecule of NO_2 diffuses to adjacent ions to form an active complex, $NO_2(NH_4^+)_2$. The active complex subsequently reacts with one molecule of NO to produce N_2 and H_2O, thus completing the catalytic cycle.

Since combustion gases usually contain water vapor and small-amounts of SO_2 even after sulfur removal processes, the effect of H_2O and SO_2 on the catalytic performance of 0.1 wt% Pt/Fe-ZSW-5 at 250 °C, was further studied in this work. When 100 ppm SO_2 and 2.5% H_2O were added to the reactants at 250 °C, the NO conversion was slightly decreased (figure 3). The NO conversion was unchanged during 8 h in the presence of water and SO_2.

The slight decrease in activity was caused by at least two factors as following: (1) The reaction temperature was low and (2) the loading of noble metal was very low, both of which limited the oxidation of SO_2 to SO_3. It is known that noble metals are good catalysts for oxidation of ammonia by O_2, N_2 and N_2O were the main products at low temperatures. They have been used for producing nitric acid from ammonia. So it is not surprising the the N_2 selectivity decreased with the addition of a noble metal. The reason for the N_2 selectivity being still very high was that Fe-ZSM-5 was also a good catalyst for N_2O decomposition. Even at room temperature, N_2O can be decomposed to N_2 and NO on Fe-ZSM-5 [36]. The small amount of noble metal would result in an also amount of N_2O formation.

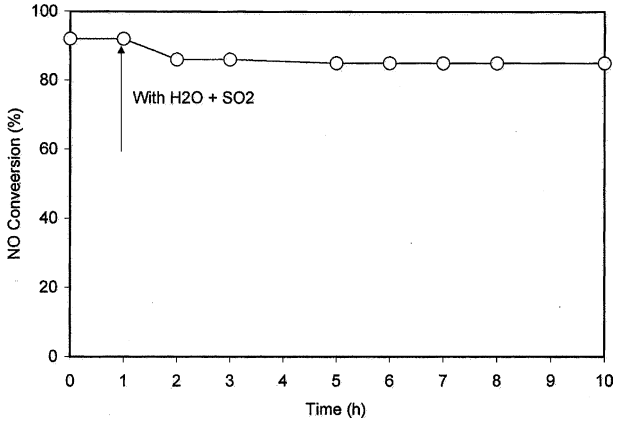

Figure 3. Effect of time-on-stream on SCR performance over 0.1 wt% Pt/Fe-ZSM-5 at 250 °C, Reaction conditions: 0.2 g catalyst, $[NH_3]$ = [NO] = 1000 ppm, $[O_2]$ = 2%, $[H_2O]$ = 2.5% (when used), $[SO_2]$ = 100 ppm (when used), He = balance, total flow rate = 500 mL/min.

Recently, Wen *et al.* [40] studied the chemical anchoring of palladium by exchanging Pd from a dilute aqueous solution of $Pd(NH_3)_4(NO_3)_2$ into either HZSM-5 or Fe-ZSM-5. They concluded that the chemical interaction of palladium with Fe ions led to a much higher dispersion of Pd particles because for Pd-ZSM-5, the Pd was present as large PdO particles, whereas in PdFe-ZSM-5, it is highly dispersed over the zeolite, Similar phenomena were also observed on Pt and Rh supported catalysts. Based on the above results it seems likely that most of the noble metals were in the pores of the zeolite and had strong interactions with the Fe ions. Temperature programmed reduction (TPR) of PdFe-ZSM-5 was also investigated by Wen *et al.* [40], and they found that the addition of palladium enhanced the reduction of iron oxides, which also indicated that strong interaction existed between noble metals and iron ions. Also, the distance between palladium and iron was probably not very far away; they should be relatively close to each other.

A summary comparison has been made for the noble metal promoted Fe-ZSM-5 catalyst with other high-activity catalysts that were reported in the literature, given in table 1. The pseudo-first-order rate constant (k) was calculated based on the first order reaction of NO, equation (1)

$$k = -\frac{F_0}{[\mathrm{NO}]_0 W}\ln(1 - X) \qquad (1)$$

where F_0 is the molar NO feed rate, $[NO]_0$ is the molar NO concentration at the inlet (at the reaction temperature), and W is the catalysts amount (g). In calculating the rate constant, it is assumed that the reaction is free of diffusion limitation, and the value of k is an indication of the relative activity of the catalyst.

From table 1, it can be seen that the activity of Pt/Fe-ZSM-5 is lower than that of Ce–Mn mixed oxides that were developed in our laboratory, but is still very high compared to other low temperature SCR catalysts shown here. This catalyst is a good candidate for low-temperature SCR of NO with ammonia.

4. Conclusion

Based on the results mentioned above, it can be concluded that the noble metal promoted Fe-ZSM-5 catalysts show good activities as well as sulfur and water resistance

Table 1
Performance of various catalysts for low-temperatures SCR of NO with NH_3

Catalyst	Feed composition			T (K)	X^c_{NO}(%)	SV (cm^3/g/h)	K^a (cm^3/g/s)	Ref.
	NO (ppm)	NH_3 (ppm)	O_2 (%)					
V_2O_5–WO_3/TiO_3	800	800	1	423	12	22,500	1.13	[34]
5%V_2O_5/AC	500	560	3.3	523	79.7	90,000	69.96	[18]
MnO_x/Al_2O_3	500	550	2	423	63	24,000	9.40	[19]
Mn_2O_3–WO_3/γ–Al_2O_3	500	550	10	423	45	91,400	21.54	[20]
15 MnNaY775[b]	1000	1000	5	443	82	48,000	33.98	[21]
10%Mn–14%Ce/USY	1000	1000	2	423	87	30,000	24.13	[29]
Fe–Mn mixed oxide	1000	1000	2	373	97	12,000	14.63	[24]
Ce–Mn Mixed oxide	1000	1000	2	423	87	150,000	120.6	[27]
MnO_x/TiO_2	2000	2000	2	373	82	10,380	6.18	[33]
Fe-ZSM-5	1000	1000	2	523	60	150,000	67.00	This work
Pt/Fe-ZSM-5	1000	1000	2	423	34	150,000	30.38	This work
	1000	1000	2	473	66	150,000	78.89	This work
	1000	1000	2	523	92	150,000	184.69	This work
Rh/Fe-ZSM-5	1000	1000	2	523	81	150,000	121.44	This work
Pd/Fe-ZSM-5	1000	1000	2	523	66	150,000	78.88	This work

[a] First-order rate constant based on equation (1).
[b] The feed contained 7% H_2O.
[c] NO conversion.

at low temperatures. On the Pt promoted Fe-ZSM-5 catalyst, nearly 90% NO conversion was reached at a very high space velocity, and a slight decrease of N_2 selectivity was observed compared to that on the Fe-ZSM-5 catalyst.

References

[1] H. Bosch and F. Janssen, Catal. Today 2 (1988) 369.
[2] H. Schneider, U. Scharf, A. Wokaun and A.. Baiker, J. Catal. 147 (1994) 545.
[3] K.C. Taylor, Catal. Rev.-Sci. Eng. 35 (1993) 457.
[4] G. Busca, L. Lietti, G. Ramis and F. Berti, Appl. Catal. B 18 (1998) 1.
[5] G. Centi and S. Perathoner, Appl. Catal. A 132 (1995) 179.
[6] M. Iwamoto and H. Yahiro, Catal. Today 22 (1994) 5.
[7] J.N. Armor, Catal. Today 26 (1995) 147.
[8] M. Shelef, Chem. Rev. 95 (1995) 209.
[9] Z.J. Li and M. Flytzani-Stephanopoulos, J. Catal. 182 (1999) 313.
[10] G.L. Bauerle, S.C. Wu and K. Nobe, Ind. Eng. Chem. Prod. Res. Dev. 17 (1978) 123.
[11] W.C. Wong and K. Nobe, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 179.
[12] F. Janssen, F. Kerkhof, H. Bosh and J.R.H. Ross, J. Phys. Chem. 91 (1987) 5921.
[13] J.W. Byrne, J.K. Chen and B.K. Speronello, Catal. Today 13 (1992) 33.
[14] G. Ramis, G. Busca and F. Bregani, Catal. Lett. 139 (1993) 353.
[15] J.P. Chen and R.T. Yang, Appl. Catal. A 80 (1992) 135.
[16] G. Busca, L. Lietti, G. Ramis and F. Berti, Appl. Catal. B 18 (1988) 1.
[17] G.L. Bauerle, S.C. Wu and K. Nobe, Ind. Eng. Chem. Prod. Res. Dev. 14 (1975) 268.
[18] J.P. Chen, R.T. Yang, M.A. Buzanowski and J.E. Cichanowicz, Ind. Eng. Chem. Res. 29 (1990) 1431.
[19] L. Singoredjo, R. Korver, F. Kapteijn and J. Moulijn, Appl. Catal. B 1 (1992) 297.
[20] Z.P. Zhu, Z.Y. Liu, H.X. Niu and S.J. Liu, J. Catal. 187 (1999) 245.
[21] P. Fabrizioli, T. Burgi and A. Baiker, J. Catal. 206 (2002) 143.
[22] M. Richter, A. Trunschke, U. Bentrup, K.-W. Brzezinka, E. Schreier, M. Schneider, M.-M. Pohl and R. Fricke, J. Catal. 206 (2002) 98.
[23] F. Notoya, C. Su, E. Sasako and S. Nojima, Ind. Eng. Chem. Res. 40 (2000) 3732.
[24] R.Q. Long, R.T. Yang and R. Chang, Chem. Commun. 5 (2002) 452.
[25] F. Kapteijn, L. Singoredjo, N.J. Dekker and J.A. Moulijn, Ind. Eng. Chem. Res. 32 (1993) 445.
[26] W.S. Kijlstra, E.K. Poels, A. Bliek, B.M. Weckhuysen and R.A. Schoonheydt, J. Phys. Chem. B 101 (1997) 309.
[27] G. Qi and R.T. Yang, J. Catal. 217 (2003) 434.
[28] G. Qi and R.T. Yang, J. Phys. Chem. B 108 (2004) 15738.
[29] G. Qi and R.T. Yang, Catal. Lett. 87 (2003) 67.
[30] G. Qi and R.T. Yang, Appl. Catal. B 44 (2003) 217.
[31] R.Q. Long and R.T. Yang, J. Am. Chem. Soc. 121 (1999) 5595.
[32] G. Qi, R.T. Yang, R. Chang, S. Cardoso and R.A. Smith, Appl. Catal. A 217 (2004) 207.
[33] P.G. Smirniotis, D.A. Peña and B.S. Uphade, Angew. Chem. Int. Ed. 40 (2001) 2479.
[34] L.J. Alemany, L. Lietti, N. Ferlazzo, P. Forzatti, G. Busca, E. Giamello and F. Bregani, J. Catal. 155 (1995) 117.
[35] E. Xue, K. Seshan and J.R.H. Ross, Appl. Catal. B 11 (1996) 65.
[36] R.Q. Long and R.T. Yang, J. Catal. 207 (2002) 224.
[37] J. Eng and C.H. Bartholomew, J. Catal. 171 (1997) 27.
[38] G. Qi and R.T. Yang, Chem. Commun. 7 (2003) 848.
[39] G. Grubert, M.J. Hudson, R.W. Joyner and M. Stockenbuber, J. Catal. 196 (2000) 126.
[40] B. Wen, J. Jia and W.M.H. Sachtler, J. Phys. Chem. B 106 (2002) 7520.