Noble metal (Pt, Rh, Pd) promoted Fe-ZSM-5 for selective catalytic oxidation of ammonia to N_2 at low temperatures

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Received 22 August 2001; accepted 8 November 2001

We have reported previously the excellent performance of Fe-exchanged ZSM-5 for selective catalytic oxidation (SCO) of ammonia to nitrogen at high temperatures (*e.g.*, 400–500 °C). The present work indicates that the reaction temperature can be decreased to 250–350 °C when a small amount of noble metal (Pt, Rh or Pd) is added (by both doping and ion exchange) to the Fe-ZSM-5. The SCO activity follows the order: Pt/Fe-ZSM-5 > Rh/Fe-ZSM-5 > Pd/Fe-ZSM-5. The noble metal promoted Fe-ZSM-5 catalysts also show higher activity for NH_3 oxidation than Ce-exchanged Fe-ZSM-5 at low temperatures. On the Pt promoted Fe-ZSM-5, near 100% of NH_3 conversion is obtained at 250 °C at a high space velocity ($\mathrm{GHSV} = 2.3 \times 10^5\ \mathrm{h}^{-1}$) and nitrogen is the main product. The presence of H_2O and SO_2 decreases the SCO performance only slightly. This catalyst is a good candidate for solving the ammonia slip problem that plagues the selective catalytic reduction (SCR) of NO with ammonia in power plants.

KEY WORDS: selective catalytic oxidation (SCO) of NH_3; selective catalytic reduction (SCR) of NO; noble metal (Pt, Rh, Pd) promoted Fe-ZSM-5; ion exchange; incipient-wetness impregnation.

1. Introduction

An efficient technology for reducing NO_x ($NO + NO_2$) emission from power plants is selective catalytic reduction (SCR) with ammonia in the presence of oxygen ($4NH_3 + 4NO + O_2 = 4N_2 + 6H_2O$). The commercial catalysts that are used today are V_2O_5 mixed with WO_3 and/or MoO_3 supported on TiO_2 due to their thermal stability and their resistance to sulfur dioxide [1]. However, one of the major concerns in this process is the emission of unreacted ammonia, resulting in a secondary air pollution problem. In order to decrease ammonia slip, most processes are carried out under the conditions of $NH_3/NO < 1$ ($\approx$0.9–0.95), *i.e.*, a tradeoff for less ammonia slip with a lower NO reduction efficiency. To achieve high NO reduction efficiencies, it is desirable to use stoichiometric or excess amount of ammonia. The residual ammonia could be removed by selective catalytic oxidation with O_2 (SCO, *i.e.*, $4NH_3 + 3O_2 = 2N_2 + 6H_2O$) to form nitrogen in a secondary bed of the SCR reactor, without introducing other reactant in the gas mixture [2]. Also, it is known that many chemical processes use reactants containing ammonia or produce ammonia as a by-product (*e.g.*, hydrodenitrogenation in petroleum-refining processes). They are all plagued by the ammonia slip problem. SCO of ammonia to nitrogen is potentially an ideal technology for removing ammonia from waste gases and consequently it has been of increasing interest in recent years [2–8].

Many catalysts have been found to be active for oxidation of NH_3 to N_2. Li and Armor [2] reported that Pt, Rh and Pd exchanged to ZSM-5 or supported on Al_2O_3 showed good SCO performance at low temperatures. The metal ion-exchanged ZSM-5 were more active and also less affected by water than the corresponding Al_2O_3 supported catalysts. Also, the noble metal catalysts were more active than V_2O_5/TiO_2 and Co-ZSM-5 [2]. For transition metal oxides supported on γ-Al_2O_3, Amblard *et al.* [3] reported that Ni, Fe, and Mn were active for the SCO reaction. Recently, we studied the SCO reaction on transition metal (Cr, Mn, Fe, Co, Ni, Cu and Pd) ion-exchanged ZSM-5 and other zeolites (*e.g.*, mordenite, clinoptilolite, Y, Beta, etc.) [7,8]. Fe-ZSM-5 showed the best SCO performance (*i.e.*, NH_3 conversion and N_2 selectivity). Near 100% of NH_3 conversion to N_2 was obtained at 450 °C at a high gas hourly space velocity ($\mathrm{GHSV} = 2.3 \times 10^5\ \mathrm{h}^{-1}$). The SCO performance on the Fe-ZSM-5 was superior to the supported transition metal oxides and noble metals. H_2O and/or SO_2 decreased the NH_3 conversion only slightly [7]. However, the maximum SCO performance of the Fe-ZSM-5 was obtained at 400–500 °C, which is higher than the temperature ($\leq$300 °C) in the down stream of vanadia catalysts for the SCR reaction. This makes it necessary to reheat the flue gas if Fe-ZSM-5 is used to remove the residual ammonia from the SCR process. One solution to this problem is to develop a low-temperature SCO catalyst that shows good performance at 250–300 °C. In this paper, we investigated the SCO performance on noble metal (Pt, Rh and Pd) promoted

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Fe-ZSM-5 because the noble metals were reported as good catalysts for oxidation of NH_3 by O_2 to form NO, N_2O and N_2 [2] and Fe-ZSM-5 was effective for the reduction of NO [9,10] and N_2O [11] with ammonia. Some of the generated N_2O and NO can be further reduced to N_2 by the unreacted NH_3, resulting in an increase in N_2 selectivity. The noble metals were added by both ion exchange and incipient-wetness impregnation techniques. The results showed that Pt/Fe-ZSM-5 was highly active in oxidation of NH_3 to N_2 at low temperatures.

2. Experimental

Fe-ZSM-5 was prepared using the conventional ion-exchange procedure [9]. Five grams of NH_4-ZSM-5 was added to 500 ml of 0.05 M $FeCl_2$ solution with constant stirring. After 24 h, the mixture was filtered and washed 5 times with deionized water. The obtained sample was first dried at 120 °C in air for 12 h and then calcined at 500 °C for 6 h. Fe^{2+} in the catalyst was oxidized to Fe^{3+} [9]. The iron content, measured by neutron activation analysis, was 1.54 wt% in the Fe-ZSM-5. NH_4-ZSM-5 ($Si/Al \approx 10$) was obtained from Alsi-Penta Zeolithe GmbH (Germany). $FeCl_2{\cdot}4H_2O$ (99%) was obtained from Aldrich.

The noble metal (Pt, Rh and Pd) doped Fe-ZSM-5 catalysts were prepared by the incipient-wetness impregnation technique, where an appropriate amount of metal solution was added to the Fe-ZSM-5. The sample was first dried at 120 °C overnight and then calcined at 500 °C for 4 h in air. The content of the noble metal was controlled at 0.5% by weight. The Pt, Rh and Pd promoted Fe-ZSM-5 catalysts were also prepared by using the ion-exchange technique. In each case, 1.2 g Fe-ZSM-5 was added to 100 ml solution containing 0.01 g noble metal with constant stirring. The pH value was adjusted to 6.0 by the use of ammonium hydroxide or nitric acid solution. After 6 h, the mixture was filtered and washed with deionized water. Again, the obtained sample was first dried at 120 °C overnight and then calcined at 500 °C for 4 h in air. According to the neutron activation analysis data, the Pt, Rh and Pd contents were 0.6 wt%, 0.06 wt% and 0.6 wt%, respectively, on Pt-Fe-ZSM-5, Rh-Fe-ZSM-5 and Pd-Fe-ZSM-5. Ce-Fe-ZSM-5 was obtained from 1.5 g Fe-ZSM-5 exchanged with 200 ml of 0.05 M $Ce(NO_3)_3$ (Aldrich, 98%) solution at room temperature [10]. The cerium content was 0.1 wt%, based on the neutron activation analysis. Finally, the obtained samples were pressed into pellets and ground to 60–100 mesh before catalytic performance test. $(NH_3)_2Pt(NO_2)_2$ (Strem Chemicals, 5 wt% Pt in ammonium hydroxide solution), $Rh(NO_3)_3$ (Aldrich, 10 wt% Rh in 5% nitric acid) and palladium(II) nitrate hydrate (Strem Chemicals, ~40% Pd) were used for noble metal sources.

The SCO performance measurement was carried out in a fixed-bed quartz reactor. The reaction temperature was controlled by an Omega (CN-2010) programmable temperature controller. A catalyst of 0.1 g was used in this work. The reactant gas was obtained by blending different gas flows. The typical reactant gas composition was as follows: 1000 ppm NH_3, 2% O_2, 500 ppm SO_2 (when used), 2.5% H_2O (when used), and balance He. The total flow rate was 500 ml/min (ambient conditions). The water vapor was generated by passing helium through a gas-wash bottle containing deionized water. The premixed gases (1.05% NH_3/He and 0.99% SO_2/He) were supplied by Matheson. A magnetic-deflection-type mass spectrometer (AERO VAC^{TM}, Vacuum Technology Inc.) was used to monitor continuously the effluent gas from the reactor, which contained NH_3 ($m/e = 17$ minus the contribution from H_2O), H_2O ($m/e = 18$), N_2 ($m/e = 28$), NO ($m/e = 30$), O_2 ($m/e = 32$) and N_2O ($m/e = 44$). NO_2 ($m/e = 46$) was not detectable with this mass spectrometer. The concentrations of the unreacted NH_3 and the generated NO_x were also continually monitored with a chemiluminescent NO/NO_x analyzer (Model 42C, Thermo Environmental Instruments Inc.). In the analyzer, a high temperature converter converted NH_3 to NO_x by the reaction $NH_3 + O_2 \rightarrow NO_x + H_2O$. The NH_3 conversion was calculated by $([NO] + 2[N_2] + 2[N_2O])/[NH_3]_0 \times 100\%$, where $[NH_3]_0$ is the initial NH_3 concentration. The selectivity is defined as the percentage conversion of ammonia to N_2, N_2O or NO. In the presence of H_2O and SO_2, only N_2 concentration/yield was monitored by the mass spectrometer because NH_3 also reacts with H_2O and SO_2/SO_3. The data were collected when the SCO reaction reached the steady state, typically after 20 min at each temperature.

3. Results and discussion

The SCO performance on Fe-ZSM-5 and Pt, Rh, Pd doped Fe-ZSM-5 is shown in figures 1 and 2. As expected, Fe-ZSM-5 showed very good catalytic performance for the SCO reaction at high temperatures. Under the conditions of 1000 ppm NH_3, 2% O_2 and $GHSV = 2.3 \times 10^5\ h^{-1}$, NH_3 conversion increased with increasing temperature and reached nearly 100% at 450–500 °C (figure 1). At low temperatures, oxidation of NH_3 to NO was not observed. N_2 was the main product (figure 2). With increasing temperature, NO formation became significant, resulting in a decrease in N_2 selectivity. However, when the reaction temperature was higher than 350 °C, it is interesting to see that NO selectivity decreased but N_2 selectivity increased significantly with temperature. This is because Fe-ZSM-5 is also a good catalyst for SCR of NO with ammonia at high temperatures [10]. The formed NO can be reduced to N_2 by the unreacted ammonia on the Fe-ZSM-5. It is noted that at low temperatures, the reactivity between NH_3 and

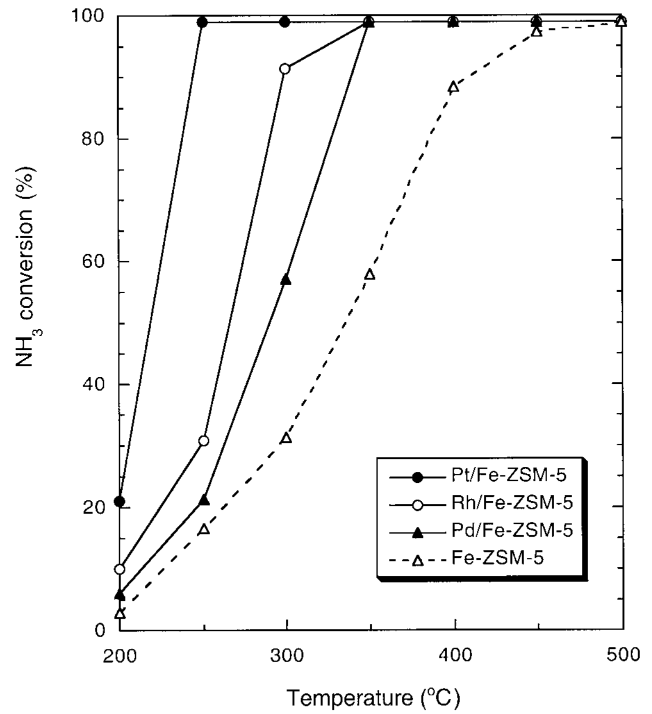

Figure 1. NH_3 conversion on 0.5 wt% Pt, Rh and Pd doped Fe-ZSM-5 catalysts. Reaction conditions: 0.1 g catalyst, $[NH_3] = 1000$ ppm, $[O_2] = 2\%$, He = balance, total flow rate = 500 ml/min and GHSV = 2.3×10^5 h^{-1}.

NO_x was not high enough to convert most of the formed NO to N_2. This results in a decrease in N_2 selectivity due to formation of NO. At 450–500 °C, nearly 100% of NH_3 was oxidized to N_2. Almost no N_2O formation was observed on the Fe-ZSM-5. When 0.5 wt% of Pt, Rh or Pd was doped on the Fe-ZSM-5, the activity for NH_3 oxidation increased significantly (figure 1). At the same temperatures (<350 °C), NH_3 conversion increased in the following order: Fe-ZSM-5 < Pd/Fe-ZSM-5 < Rh/Fe-ZSM-5 < Pt/Fe-ZSM-5. On the 0.5 wt% Pt/Fe-ZSM-5, near 100% of NH_3 conversion was obtained at 250 °C, which was 200–250 °C lower than that on the Fe-ZSM-5. It is clear that the addition of noble metals decreased reaction temperature for ammonia oxidation. As compared to Fe-ZSM-5, the noble metal doped Fe-ZSM-5 catalysts showed lower N_2 selectivity for ammonia oxidation. The N_2 selectivity decreased with increasing temperature (figure 2). More N_2O and NO were generated at higher temperatures. The maximum N_2 yield was 84–90% on the noble metal doped Fe-ZSM-5.

The noble metals were also added to Fe-ZSM-5 by ion-exchange technique. The SCO performance on the Pt-Fe-ZSM-5, Rh-Fe-ZSM-5 and Pd-Fe-ZSM-5 is summarized in table 1. Their catalytic activities were similar to those on the corresponding noble metal doped catalysts. Pt-Fe-ZSM-5 was highly active for ammonia oxidation. NH_3 conversion reached nearly 100% when the reaction temperature was above 250 °C. N_2 selectivity decreased with increasing temperature: 83–99% of N_2 selectivity was obtained at 200–400 °C and the other products were NO and N_2O. By comparison, Pd-Fe-ZSM-5 showed lower NH_3 conversion than Pt-Fe-ZSM-5 under the same conditions. The lowest SCO activity was obtained on the Rh-Fe-ZSM-5 due to a very low Rh content.

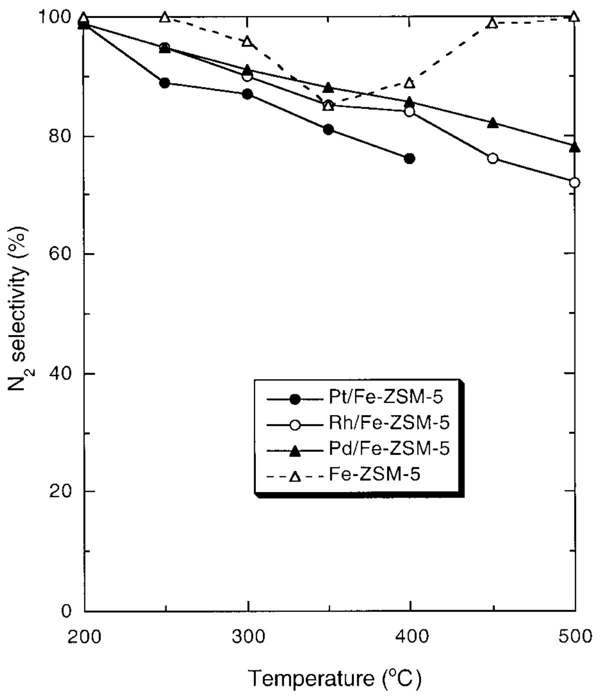

Figure 2. N_2 selectivity on 0.5 wt% Pt (or Rh, Pd) doped Fe-ZSM-5 catalysts. Reaction conditions are the same as those in figure 1.

Cerium ions also showed a promoting role for the ammonia SCO reaction. When Ce^{3+} ions were exchanged to Fe-ZSM-5, the SCO performance was increased at low temperatures as compared to Fe-ZSM-5 (table 1). The noble metal promoted Fe-ZSM-5 showed higher activity for ammonia oxidation than the cerium promoted Fe-ZSM-5 at low temperatures, whereas Ce-Fe-ZSM-5 showed higher N_2 selectivity than the former (table 1).

Since the waste streams usually contain water vapor and small amounts of SO_2, we further studied the effect of H_2O and SO_2 on the catalytic performance of 0.5 wt% Pt/Fe-ZSM-5. Since the unreacted ammonia will react with H_2O and SO_2/SO_3 to generate ammonium sulfite/sulfate or bisulfite/bisulfate, it is difficult to analyze the real ammonia concentration before and after the reaction. We used product N_2 yield (detected by the mass spectrometer) for SCO performance here. When 500 ppm SO_2 and 2.5% H_2O were added to the reactants at 350 °C, SCO performance was inhibited only slightly (figure 3). N_2 yield was almost unchanged during 3 h on stream in the presence of H_2O and SO_2.

Our previous work on Fe-ZSM-5 showed its excellent SCO performances at high temperatures [7,8]. The present work indicated that the reaction temperature could be decreased to 250–350 °C when a small amount of noble metal (Pt, Rh or Pd) was added to the Fe-ZSM-5. Among them, Pt showed the best promoting

Table 1
SCO performance on Pt, Rh, Pd, Ce-exchanged Fe-ZSM-5[a]

Catalyst[b]	Temperature (°C)	NH_3 conversion (%)	Selectivity (%)			N_2 yield (%)
			N_2	N_2O	NO	
Pt(0.6%)-Fe-ZSM-5	200	45	99	1	0	45
	250	99	92	8	0	91
	300	99	90	5	5	89
	350	99	88	3	9	87
	400	99	83	0	17	82
Rh(0.06%)-Fe-ZSM-5	200	4	100	0	0	4
	250	15	95	1	4	14
	300	33	91	6	3	30
	350	75	88	2	10	66
	400	99	90	4	6	89
Pd(0.6%)-Fe-ZSM-5	200	6	99	0	1	6
	250	19	91	8	1	17
	300	72	90	7	3	65
	350	99	88	8	4	87
	400	99	86	8	6	85
Ce(0.1%)-Fe-ZSM-5	300	51	96	0	4	49
	350	93	98	0	2	91
	400	98	100	0	0	98
	450	99	89	0	11	88

[a] Reaction conditions: 0.1 g catalyst, $[NH_3] = 1000$ ppm, $[O_2] = 2\%$, He = balance, total flow rate = 500 ml/min and GHSV = $2.3 \times 10^5\ h^{-1}$.

[b] For catalyst designation, the number in parentheses indicates the metal content by weight.

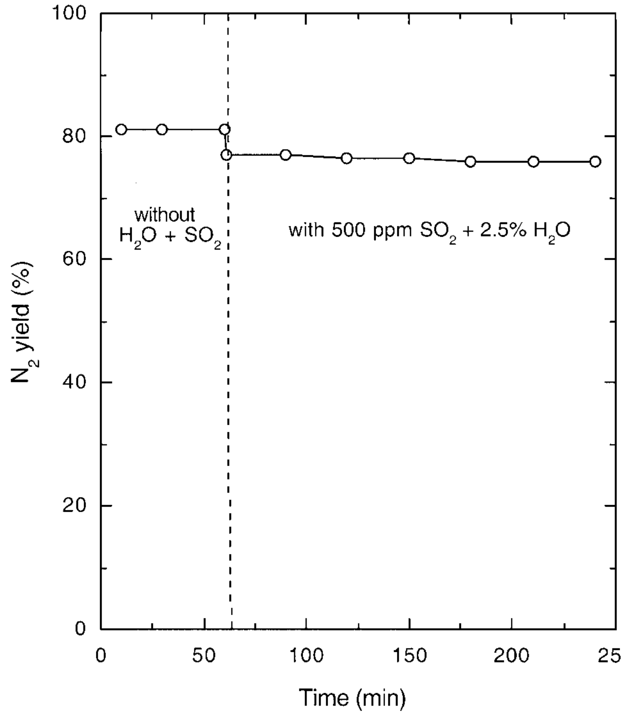

Figure 3. Effect of time-on-stream on SCO performance over 0.5 wt% Pt/Fe-ZSM-5 at 350 °C. Reaction conditions: 0.1 g catalyst, $[NH_3] = 1000$ ppm, $[O_2] = 2\%$, $[H_2O] = 2.5\%$ (when used), $[SO_2] = 500$ ppm (when used), He = balance, total flow rate = 500 ml/min and GHSV = $2.3 \times 10^5\ h^{-1}$.

role. On the Pt promoted Fe-ZSM-5, near 100% of NH_3 conversion was obtained at 250 °C at a high space velocity (GHSV = $2.3 \times 10^5\ h^{-1}$). The oxidation products were N_2, N_2O and NO, with N_2 as the major product. It is known that the noble metals are good catalysts for oxidation of NH_3 by O_2. N_2 and N_2O are the main products at low temperatures but NO is the main product at high temperatures [12]. They have been used commercially for producing nitric acid from NH_3 (at high temperatures, *e.g.*, 800 °C). The noble metals on the catalyst surface provide active sites for oxidation of NH_3 to NO, N_2O and N_2. Since Fe-ZSM-5 is a good catalyst for SCR of NO [10] and N_2O [11] with ammonia, some of the N_2O and NO generated by oxidation can be further reduced to N_2 by the unreacted NH_3. Simultaneously, this will improve ammonia conversion and increase N_2 selectivity. On the other hand, Fe-ZSM-5 also contributes toward NH_3 oxidation: 16–58% NH_3 conversions were obtained at 250–350 °C on the pure Fe-ZSM-5 (figure 1). Li and Armor [2] reported that Pt, Rh and Pd exchanged ZSM-5 showed good activity for ammonia oxidation at low temperatures. But their N_2O selectivity was very high when most of the ammonia was converted. For example, 58–61% of N_2O selectivity on Pt-ZSM-5 (with 2.55 wt% Pt) and 16–25% on Pd-ZSM-5 (with 4.01 wt% Pd) were obtained at 250–300 °C. By comparison, much lower N_2O selectivity

(<10%) was obtained on the noble metal promoted Fe-ZSM-5 catalysts as shown in this work. This is probably due to the fact that Fe-ZSM-5 is a good catalyst for N_2O decomposition [13,14] and N_2O reduction with NH_3 [11]. Even at room temperature, N_2O can be decomposed into N_2 and NO on the Fe-ZSM-5 [14]. The decomposition and/or reduction of N_2O on the Fe-ZSM-5 decreased N_2O selectivity as compared to ZSM-5. Also, a smaller amount of noble metals on the catalysts in this work (0.06–0.6 wt% *versus* 2.55–4.01 wt% in ref. [2]) would result in less N_2O formation.

4. Conclusions

Based on the above results, it can be concluded that noble metal (Pt, Rh and Pd) promoted Fe-ZSM-5 showed good SCO performance at low temperatures. The promoting role increased in the following sequence: Pd < Rh < Pt. On the Pt promoted Fe-ZSM-5, near 100% of NH_3 conversion was obtained at 250 °C at a high space velocity. The oxidation products were N_2, N_2O and NO, with N_2 as major product. The presence of H_2O and SO_2 decreased its activity only slightly.

Acknowledgment

We gratefully acknowledge Dr. Ramsay Chang of EPRI for discussions.

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