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Superior ion-exchanged ZSM-5 catalysts for selective catalytic oxidation of ammonia to nitrogen

Richard Q. Long and Ralph T. Yang*

Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA.
E-mail: yang@umich.edu

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Fe-ZSM-5 showed the best catalytic performance (nearly 100% N_2 yield) and resistance to water vapor for selective catalytic oxidation of NH_3 to N_2 at a high gas hourly space velocity (2.3×10^5 h^{-1}) among transition-metal (Cr, Mn, Fe, Co, Ni and Cu) ion-exchanged ZSM-5 catalysts.

The removal of ammonia from waste streams is becoming an increasingly important issue due to environmental reasons. Many chemical processes use reactants containing ammonia or produce ammonia as a by-product. They are all plagued with the ammonia slip problem. Selective catalytic oxidation (SCO) of ammonia to nitrogen is potentially an ideal technology for removing ammonia from oxygen-containing waste gases and consequently it is of increasing interest in recent years.[1–12] The SCO process could also be applied to the selective catalytic reduction (SCR) of NO by ammonia where ammonia slip has been a serious problem,[2] as well as to the combustion of biomass-derived gases for removing the NH_3 impurity.[3-5]

Early results[1] on ammonia oxidation showed that noble metals (*e.g.* Pt and Pd) were active for oxidation of NH_3 to NO and N_2O, while transition metal oxides such as V_2O_5 could selectively convert NH_3 to N_2, but were much less active than the noble metals. Li and Armor[2] reported that Pt, Rh and Pd exchanged to ZSM-5 or supported on Al_2O_3 showed good SCO performance in a wet stream, which were more active than V_2O_5/TiO_2 and Co-ZSM-5. More recently, Burch and Southward found that 12-tungstophosphoric acid[4] and Ni, Fe and Mn oxides supported on γ-Al_2O_3[5] were active for the reaction. A number of other catalysts were also investigated, such as $CuMoO_4$,[6] CuO/Al_2O_3,[7,8] Cu, Co and Ni oxides doped on SiO_2,[9] Cu–Mn/TiO_2,[10] V_2O_5/TiO_2, CuO/TiO_2 and Cu-ZSM-5,[11] as well as V_2O_5, MoO_3 and WO_3 on various supports.[12] They all exhited activities for N_2 formation under different conditions. However, the aforementioned work was normally performed at low space velocities ($< 10^5$ h^{-1}) and in the absence of H_2O or SO_2. Here, we report a series of transition metal (*i.e.* Cr, Mn, Fe, Co, Ni and Cu) ion-exchanged ZSM-5 samples that have excellent catalytic performance (both activity and product selectivity) for the SCO reaction at a high space velocity. The effects of H_2O and/or SO_2 are also studied.

Transition metal ion-exchanged ZSM-5 samples were prepared using the conventional ion exchange procedure. NH_4-ZSM-5 (Si/Al $\approx$ 10) was obtained from Alsi-Penta Zeolithe Gmbh (Germany). In each experiment, 2 g NH_4-ZSM-5 was added to 200 ml of 0.05 M $Cr(MeCO_2)_3$, $Mn(MeCO_2)_2$, $FeCl_2$, $Co(MeCO_2)_2$, $Ni(MeCO_2)_2$ or $Cu(MeCO_2)_2$ solution with constant stirring at room temperature. After 24 h, the particles were filtered off and washed with deionized water. Pd-ZSM-5 was prepared by exchanging NH_4-ZSM-5 with 100 ml 0.015 M $Pd(NO_3)_2$ solution at room temperature for 24 h.[2] The obtained samples were first dried at 120 °C in air for 12 h, then calcined at 500 °C for 6 h. H-ZSM-5 was prepared by calcining NH_4-ZSM-5 at 500 °C for 3 h. The metal contents measured by neutron activation analysis in the Cr, Mn, Fe, Co, Ni, Cu and Pd ion-exchanged ZSM-5 samples were 0,13, 1.03, 1.59, 1.24, 0.85, 4.35 and 5.51% by weight, respectively.

The SCO performance tests were carried out in a fixed-bed quartz reactor described elsewhere.[13] The typical reaction conditions were as follows: 0.1 g (0.13 ml) catalyst, 1000 ppm NH_3, 2% O_2, 500 ppm SO_2 (when used), 4% water vapor (when used) and balance He. The total flow rate was 500 ml min^{-1} (ambient conditions) and thus a high gas hourly space velocity (GHSV = 2.3×10^5 h^{-1}) was obtained. Premixed gases (1.05% 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 deionized water. The tubings of the reactor system were heat traced with heating tapes to prevent formation and deposition of ammonium sulfate/hydrogensulfate. A magnetic deflection type mass spectrometer (AERO VAC™, Vacuum Technology Inc.) was used to monitor continuously the effluent gas from the reactor. The concentrations of unreacted NH_3 and formed NO_x (NO + NO_2) were also continually monitored by a chemiluminescent NO/NO_x analyzer (Thermo Electro Corporation, Model 10), where a high temperature converter oxidized NH_3 to NO_x by the reaction $NH_3 + O_2 \rightarrow NO_x + H_2O$.

The catalytic performances of different ion-exchanged ZSM-5 catalysts are summarized in Table 1. H-ZSM-5 showed a good activity for NH_3 oxidation at 350–450 °C, with 62–74% selectivity for N_2 and 23–37% selectivity for NO. N_2 selectivity increased slightly with temperature. It is noted that a moderate

Table 1 Catalytic performance of ion-exchanged ZSM-5 catalysts[a]

Catalyst	T/°C	NH_3 conv. (%)	Selectivity (%)			N_2 yield (%)
			N_2	N_2O	NO	
Empty tube	350	23	51	1	48	12
	400	37	43	2	55	16
	450	55	35	1	64	19
H-ZSM-5	350	52	74	3	23	38
	400	80	73	2	25	58
	450	88	62	1	37	55
Cr-ZSM-5	350	72	75	2	23	54
	400	83	77	2	21	64
	450	96	94	1	5	90
Mn-ZSM-5	350	68	77	3	20	52
	400	81	47	4	49	38
	450	82	40	3	57	33
Fe-ZSM-5	350	63	92	0	8	58
	400	95	98	0	2	93
	450	99	100	0	0	99
Co-ZSM-5	350	58	73	4	23	42
	400	61	59	1	40	36
	450	70	49	0	51	34
Ni-ZSM-5	350	39	69	4	27	27
	400	51	62	2	36	32
	450	63	60	0	40	38
Cu-ZSM-5	350	48	95	2	3	46
	400	95	98	1	1	93
	450	97	100	0	0	97
Pd-ZSM-5	300	80	73	19	8	58
	350	92	73	17	10	67
	400	90	63	18	19	57

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

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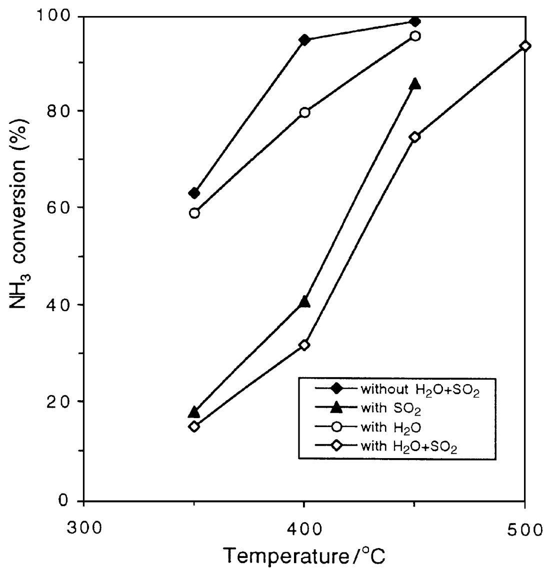

Fig. 1 Effect of H_2O and SO_2 on NH_3 conversion for Fe-ZSM-5. *Reaction conditions*: 0.1 g catalyst, $[NH_3] = 1000$ ppm, $[O_2] = 2\%$, 500 ppm SO_2 (when used), 4% water vapor (when used), He = balance, total flow rate = 500 ml min^{-1} and GHSV = 2.3×10^5 h^{-1}.

activity was also observed on the empty reactor under the same conditions, resulting from homogeneous NH_3 oxidation, but the major product was NO (Table 1). When transition metal ions were exchanged to ZSM-5, Cr-ZSM-5, Fe-ZSM-5 and Cu-ZSM-5 showed very high activities for oxidation of NH_3 to N_2. Only small amounts of N_2O and NO were produced by Fe-ZSM-5 and Cu-ZSM-5 catalysts. Both NH_3 oxidation activity and N_2 selectivity increased with temperature. Near 100% N_2 yield was obtained on Fe-ZSM-5 at 450 °C. In comparison, a lower activity was observed on Mn-ZSM-5, Co-ZSM-5 and Ni-ZSM-5, with large amounts of NO formation. These results suggest that metal cations in the ZSM-5 play an important role in the SCO of NH_3 to N_2. Pd-ZSM-5, a good SCO catalyst reported by Li and Armor,[2] also showed high NH_3 conversions under our reaction conditions, *i.e.* a higher space velocity (2.3×10^5 h^{-1} *vs.* 4.6×10^4 h^{-1} in ref. 2), but the selectivity for N_2 was lower than that on Fe-ZSM-5 and Cu-ZSM-5. The maximum N_2 yield on the above catalysts increased in the sequence of Co-ZSM-5 ≈ Ni-ZSM-5 < Mn-ZSM-5 < H-ZSM-5 < Pd-ZSM-5 < Cr-ZSM-5 < Cu-ZSM-5 < Fe-ZSM-5. This rank order is similar to the previous results obtained on the metal ion-exchanged Y zeolites, except for Fe.[1] The nitrogen balance was above 95% in this work.

It is known that the waste streams usually contain water vapor and small amounts of SO_2. We further studied the effects of H_2O and SO_2 on the catalytic performance of Cr-ZSM-5, Fe-ZSM-5 and Cu-ZSM-5. For Cr-ZSM-5, when 500 ppm SO_2 and/or 4% H_2O were added to the reactants, NH_3 conversion decreased significantly. Only 50% NH_3 conversion was obtained at 450 °C in the presence of both H_2O and SO_2. Comparatively, NH_3 conversion was decreased only slightly by H_2O on Fe-ZSM-5 (Fig. 1). SO_2 and $H_2O + SO_2$ decreased NH_3 conversion at 350–450 °C, but the decrease was less significant at high temperatures. For example, 94% NH_3 conversion could be obtained at 500 °C. H_2O and SO_2 also inhibited NH_3 conversion over Cu-ZSM-5. Only 65% NH_3 conversion was observed at 450 °C in the presence of H_2O and SO_2. Increasing the temperature to 500 °C resulted in 73% NH_3 conversion. N_2 was the dominant product for NH_3 oxidation in the presence of H_2O and/or SO_2.

The above results indicate that Fe, Cu and Cr ion-exchanged ZSM-5 are very active for selective catalytic oxidation of NH_3 to N_2. Our previous results showed that, although iron cations were exchanged with NH_4-ZSM-5 as Fe^{2+}, most iron cations in the Fe-ZSM-5 are present as Fe^{3+} ions after calcination, leaving only a small amount of Fe^{2+}.[14] An equilibration between Fe^{2+} and Fe^{3+} exists in the Fe-ZSM-5. It has also been reported that both Cu^+ and Cu^{2+} ions are present in Cu-ZSM-5[15] and the ratio of Cu^+/Cu^{2+} depends on the Cu content and the preparation procedure. The variable valence of metal cations in these two catalysts may be beneficial to oxygen adsorption and activation. Therefore, a high activity for the SCO reaction is expected. Relatively lower activities were observed on Mn, Co, and Ni ion-exchanged ZSM-5. This may be attributed to their stabilized valence in zeolites,[1] which is not favorable for oxygen activation. H_2O and SO_2 have strong negative effects on NH_3 conversion for Cr-ZSM-5 and Cu-ZSM-5, whereas H_2O decreased NH_3 conversion slightly for Fe-ZSM-5. Although SO_2 decreased NH_3 conversion at low temperatures for Fe-ZSM-5, a high NH_3 conversion (94%) was obtained at 500 °C in the presence of H_2O and SO_2 at such a high space velocity (GHSV = 2.3×10^5 h^{-1}). Fe-ZSM-5 may be suitable as a practical catalyst for oxidation of NH_3 to N_2 in a wet stream. In addition, the effects of the ammonia concentration on activity and other Fe-exchanged zeolites were also studied for the SCO reaction. The initial results showed that NH_3 conversion over Fe-ZSM-5 increased with a decrease in NH_3 concentration. For example, 99% NH_3 conversion was obtained at 350 °C when the NH_3 concentration was decreased to 10 ppm (*vs.* 63% at 1000 ppm). Also, the SCO performance was found to follow the trend Fe-ZSM-5 ≈ Fe-mordenite ≈ Fe-clinoptilolite > Fe-Y ≈ Fe-beta > Fe-ferrierite ≈ Fe-chabazite. More details will be presented in a future paper. Moreover, Fe-ZSM-5 is also a good catalyst for the selective catalytic reduction (SCR) of NO with ammonia.[13] In the SCR reaction, the reactions of NH_3 with NO/O_2 and that with O_2 are known as two competitive reactions. A decrease in reactivity of NH_3 with O_2 by $H_2O + SO_2$ will be beneficial to NO reduction, which has indeed been observed in our previous results that $H_2O + SO_2$ increased the SCR activity at high temperatures on Fe-ZSM-5.[13]

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