ELSEVIER

Catalysis Today 61 (2000) 179–185

CATALYSIS TODAY

www.elsevier.com/locate/cattod

NH_3 oxidation to nitrogen and water at low temperatures using supported transition metal catalysts

Lu Gang*, B.G. Anderson, J. van Grondelle, R.A. van Santen

Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology,
PO Box 513, Eindhoven 5600 MB, Netherlands

Abstract

The ability of several alumina-supported metal catalysts and transition-metal ion-exchanged zeolite Y catalysts to oxidize ammonia to nitrogen and water at low temperatures (between 200 and 350°C) was tested both at high and low ammonia concentrations. Copper-containing zeolite Y catalysts were comparable in activity and were more selective than noble-metal containing zeolite catalysts of similar metal loading. Cu/zeolite-Y catalysts were superior to copper/molybdenum and vanadium/alumina catalysts. Postsynthesis treatment of Cu/zeolite-Y with NaOH increased the activity for ammonia oxidation; dispersion and size of the supported copper-oxide particles were very important parameters. Co-fed steam dramatically increased the deactivation on all catalysts, especially at lower temperatures. © 2000 Published by Elsevier Science B.V.

Keywords: Ammonia; Oxidation; Copper-zeolite Y; Copper catalyst; Copper oxide

1. Introduction

The removal of ammonia from air or water is environmentally important. Currently, ammonia is removed from industrial flue gases via biological treatment by absorption, or by thermal combustion. An attractive alternative process is the use of selective catalytic oxidation to nitrogen and water. Such technology may also find application in combination with the selective catalytic reduction (SCR) process in which NO_x is reduced to nitrogen using ammonia. At present unreacted ammonia is present in the off-gas and must therefore be removed in a secondary step [1,2].

Early research involving ammonia oxidation has been reviewed and the activities of several metals and metal oxides for nitrogen and NO_x formation at low temperature have been systematically compared [3]. Most of these studies involved either single polycrystalline metals or simple metal oxides. Supported metals, supported metal oxides, metal alloys, and mixed metal oxides have been studied to a lesser extent. Several papers have been published regarding the ammonia oxidation over alumina-supported platinum catalysts [4–6]. It was discovered that significant deactivation occurred on these catalysts at temperatures below 200°C. To date zeolite Y is to our knowledge the only zeolite studied in some detail for this reaction [7]. Some initial screening studies have also been reported for ZSM-5 [8]. Investigations involving ammonia oxidation on V_2O_5, WO_3 and MoO_3, themselves supported on various metal oxides, at temperatures between 300 and 400°C have been reported [9–15]. Of these, the best catalyst reported was a silica-supported PbO-promoted, molybdenum catalyst on which ammonia could be oxidized with 100% selectivity to nitrogen at temperatures of about 400°C [13]. Li and Armor [16] studied the selective NH_3

---

* Corresponding author. Fax: +31-40-245-5054.
E-mail address: l.gang@chem.tue.nl (L. Gang).

PII: S0920-5861(00)00375-8

oxidation to N_2 in wet streams over ion-exchanged ZSM-5 and alumina-supported Pd, Rh and Pt catalysts at 200–350°C. They concluded that the ammonia conversion was not affected by co-feeding steam at high temperatures, but was decreased at lower temperatures (200–250°C) when 5 vol.% water vapor was added. Generally, ion-exchanged ZSM-5 catalysts were more active than alumina-supported catalysts of identical metal loadings and were less affected by the addition of water vapor. The selectivity to N_2 was observed to be relatively high on Rh and Pd catalysts, but was low on Pt catalysts. Wollner and Lange [17] reported that high degree of ammonia conversion (80–100%) could be obtained over mixed copper/manganese oxides supported on titania at temperatures higher than about 300°C. Unfortunately the selectivity of this process was not clearly reported.

The above studies show that noble-metals such as platinum are very active for ammonia oxidation but form large amount of nitrogen oxides. Although supported molybdenum and vanadium catalysts show very promising selectivity, the reaction temperature needed is too high to be matched with some industrial applications. The aim of this study is the development of active new catalytic materials that are capable of selective oxidation of ammonia to nitrogen at low temperatures. For this purpose we have screened the performance of several transition-metals deposited either onto alumina (by incipient wetness impregnation) or onto sodium zeolite Y by ion exchange. The results obtained are reported below.

2. Experimental

2.1. Catalyst preparation

Ion-exchanged CuNaY, CoNaY, AgNaY, ZnNaY, MnNaY and FeNaY catalysts. Ion exchange was performed using: $Cu(NO_3)_2{\cdot}3H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $AgNO_3$, $Zn(NO_3)_2{\cdot}6H_2O$, $MnSO_4{\cdot}H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$. In most cases the sodium form of zeolite Y (NaY) (10 g) was stirred for 24 h at room temperature in aqueous solutions (400 ml, dissolved metal salt concentration adjusted to match 100% Na ion exchange). In the case of Fe/Na ion exchange, only 2 h of stirring were required. The slurry was then filtered and the solid was washed three times with deionized, distilled water and oven-dried at 110°C overnight. Catalysts were made into pellets by compressing the powder using 10 t pressure (250–425 μm particles). The catalysts were activated at 400°C for 2 h in a flow of oxygen/helium (20/80 v/v) before catalyst testing.

Alumina-supported Cu, Mo, V, Pt, Ir, Rh, Pd catalysts. These catalysts were prepared by incipient wetness impregnation. The precursors were: $Cu(NO_3)_2{\cdot}3H_2O$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, NH_4VO_3, H_2PtCl_6, $IrCl_3{\cdot}3H_2O$, $Rh(NO_3)_3$, $PdCl_2$. Metal loadings (wt.%) were: 5–15, 15, 10, 5–15, 1.2, 1.2, and 1.2%, respectively. All catalysts were calcined in flowing air at 600°C for 24 h before testing.

2.2. Catalyst testing

Catalytic activity measurements were carried out in a quartz-tube, fixed-bed reactor (4 mm internal diameter). About 0.2 g catalyst was used (250–425 μm particles). Experiments were performed using either an excess of ammonia or an excess of oxygen. Ammonia, oxygen and helium flow rates were controlled using mass-flow meters. Water vapor was introduced by passing the helium flow through a water saturator at elevated temperature (T=50°C). The inlet and outlet gas compositions were analyzed by a gas chromatograph equipped with a thermal conductivity detector. A quadruple mass spectrometer was also used to distinguish different products.

3. Results and discussion

3.1. Zeolite-based catalysts

Various ion-exchanged Na zeolite Y catalysts were tested and the resulting ammonia conversion and nitrogen selectivity data are shown in Table 1. Clearly, only CuY is very active and selective for ammonia oxidation. All other ion-exchanged catalysts had almost no activity, in fact they are worse than NaY itself. This is quite different from the simple metal-oxide catalysts published in the literature.

Ione et al. [18] and Schoonheydt et al. [19] reported that the polynuclear nickel or copper ion complexes were formed in the framework of zeolite Y when NaY was ion exchanged with aqueous $Ni(NO_3)_2$ or

Table 1
Activity of various transition-metal ion-exchanged zeolite Y catalysts for ammonia oxidation[a]

Catalyst	Temperature (°C)	NH_3 conversion (%)	N_2 selectivity (%)
CuY	400	94	98
NaY	400	18	99
CoY	400	4.5	–
AgY	400	0.6	–
ZnY	400	2.3	–
MnY	400	1.7	–
FeY	400	13	96

[a] Reaction conditions: NH_3: 1.33 vol.%; O_2: 0.91 vol.%; H_2O: 2.08 vol.%; flow rate=30.7 N ml/min; catalyst weight=0.2 g.

$Cu(NO_3)_2$ solution at pH 6–7. These polynuclear cations gave a higher activity for CO oxidation than the mononuclear ions. Suzuki et al. [20,21] also successfully prepared an excellent CO oxidation catalyst of highly dispersed, nickel-oxide catalyst by hydrolyzing a Ni^{2+}-exchanged zeolite Y with either aqueous NaOH or ammonia solution at different pH values. We were curious to see the effect that such NaOH treatment would have on the ammonia oxidation reaction. Table 2 shows the resulting conversion and selectivity data obtained following treatment of zeolite-based catalysts with NaOH solutions (pH=10) following ion exchange. This treatment procedure was the same as proposed by Suzuki et al.

The activity of all metal zeolite catalysts for ammonia oxidation increased drastically following this NaOH treatment. This significantly higher activity was apparently induced by the formation of small metal-oxide particles in the zeolite. As can be seen in Fig. 1, there are two peaks for O_2 TPD profiles on 8.4 wt.% copper ion-exchanged zeolite Y (CuY-8.4) catalyst. Since no O_2 desorption is observed on NaY, these two O_2 desorption peaks must involve Cu on the zeolite. Following NaOH treatment the amount of O_2 desorbed was greatly increased. Many studies on the complete oxidation of CO and of hydrocarbons have shown that the activity is directly dependent on the amount of adsorbed oxygen [22,23]. This increased oxygen adsorption capacity of the catalyst following NaOH treatment may be the reason for the enhanced performance in ammonia oxidation.

Table 2
The effect of postsynthesis NaOH treatment on the zeolite Y catalysts[a]

Catalyst	Temperature (°C)	NH_3 conversion (%)	N_2 selectivity (%)
CuY (3.7 wt.%)	250	16	97
	300	54	98
CuY (8.4 wt.%)	250	25	97
	300	88	97
CuY (3.7 wt.%, after NaOH treatment)	200	19	97
	250	56	97
	300	100	98
CuY (8.4 wt.%, after NaOH treatment)	200	35	95
	250	68	97
	300	100	98
AgY (after NaOH treatment)	250	11	75
	300	81	80
CoY (after NaOH treatment)	250	14	71
	300	42	75

[a] Reaction conditions: NH_3: 1.14 vol.%; O_2: 8.21 vol.%; flow rate=74.7 N ml/min; catalyst weight=0.2 g.

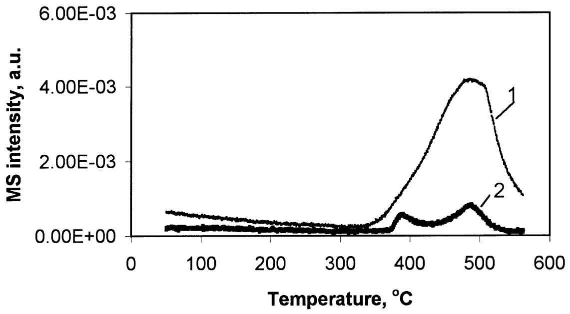

Fig. 1. Temperature-programmed O_2 desorption profiles obtained on CuY (8.4 wt.%) catalysts with (1) and without (2) treatment using NaOH following ion exchange (desorption in flowing He (50 N ml/min), ramp rate=10°C/min, catalyst weight=0.6 g).

3.2. Alumina-supported metal catalysts

Metal particle size is known to be an important parameter in the activity of catalysts for ammonia oxidation. The size of metal particles on alumina can be easily controlled by varying the metal loading, the calcination temperature, or the calcination time. Several such experiments were performed on alumina-supported metal catalysts, the results are shown in Table 3. It can be seen that alumina-supported copper catalysts are also very active for ammonia oxidation. There exists an optimal metal loading that may indicate that copper dispersion becomes poorer on alumina at metal loading higher than ca. 10 wt.%. Indeed, results previously obtained by us using high-resolution transmission electron microscopy (HREM) and ultraviolet spectroscopy revealed the absence of either copper or copper-oxide particles of detectable size on alumina at loadings of 10 wt.% or lower [24]. However, small particles of CuO were detected at 15 wt.%. The fact that zeolite-based copper catalysts are superior to alumina-supported copper catalysts may be attributable to the high dispersion of copper in the zeolite. As shown in Table 3, the conventionally used supported-molybdenum and supported-vanadium catalysts cannot compete with copper catalysts at low temperature.

3.3. The stability of catalysts

Fig. 2 shows the measured NH_3 conversion vs. time on stream at various temperatures for Cu ion-exchanged catalysts. It can be seen from the figure that the catalysts were fairly stable. Catalysts subjected to NaOH treatment showed a slight initial deactivation at 250°C, but at 200°C deactivation disappeared. The CuY catalyst untreated by NaOH showed a very stable activity, perhaps even a slight increase in activity with time. Large initial deactivation was observed for alumina-supported copper and for the reduced noble-metal catalysts (see Fig. 3) during similar ammonia oxidation experiments. As all of the alumina-based catalysts were calcinated at high temperature and there were no hydrocarbons in

Table 3
Activity of various alumina-supported transition-metal catalysts for ammonia oxidation[a]

Catalyst	Temperature (°C)	NH_3 conversion (%)	N_2 selectivity (%)
Cu/Al_2O_3 (5 wt.%)	250	0	–
	300	21	97
	350	75	96
Cu/Al_2O_3 (10 wt.%)	250	15	97
	300	90	96
	350	100	90
Cu/Al_2O_3 (15 wt.%)	250	9	97
	300	46	96
	350	100	94
Mo/Al_2O_3 (15 wt.%)	300	8	88
	400	74	89
V/Al_2O_3 (10 wt.%)	400	45	95

[a] Reaction conditions: NH_3: 1.14 vol.%; O_2: 8.21 vol.%; flow rate=74.7 N ml/min; catalyst weight=0.2 g.

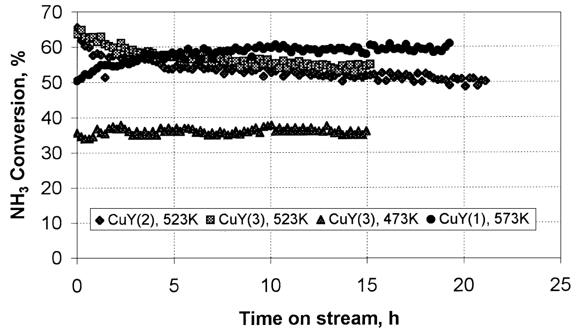

Fig. 2. The stability of Cu-zeolite Y catalysts: NH_3 conversion vs. time on stream at different reaction temperatures. CuY(1): ion exchanged with 8.4 wt.% loading; CuY(2): after NaOH treatment, 3.7 wt.%; CuY(3): after NaOH treatment, 8.4 wt.%. Reaction conditions: NH_3: 1.14 vol.%; O_2: 8.21 vol.%; flow rate=74.7 N ml/min; catalyst weight=0.2 g.

the reaction system, metal sintering and coking were excluded as possible causes of this deactivation. The most probable reason for deactivation is either reconstruction of the metal surface or a change of the chemical state of the surface.

3.4. *Effect of O_2/NH_3 ratio and water vapor*

The O_2/NH_3 ratio had a large effect on both the activity and selectivity of all catalysts. Increasing the O_2/NH_3 ratio increased the activity but decreased the selectivity (see Table 4). Co-fed steam in the feed gas lowered the activity of the catalysts at low temperatures but had less effect at high temperatures (see Table 5). Since the ammonia oxidation reaction is irreversible, water should have no effect on this reaction from thermodynamic point of view. This effect may be caused by the adsorption of water or by condensation of water on the catalysts resulting in partial blocking of the active sites.

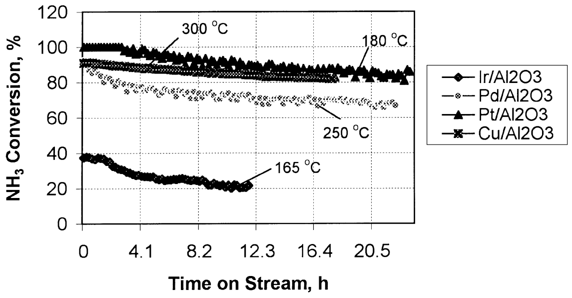

Fig. 3. The stability of various alumina-supported, transition-metal catalysts during ammonia oxidation at different temperatures (NH_3/O_2=0.14 v/v, WHSV=22 500 h^{-1}, $[NH_3]$=11 400 ppm in He, catalyst weight=0.2g).

3.5. *Effect of ammonia concentration*

In recent years considerable attention has been focused on the catalytic removal of ammonia from flue gases. The ammonia concentration in such exhaust streams is often quite low (<1000 ppm). Since the surface concentration of nitrogen-containing substances plays an important role in the selectivity of ammonia oxidation, some influence of NH_3 concentration on the activity and selectivity of the catalyst may be expected. It has been previously shown, over supported-molybdenum catalysts [15], that both the activity and selectivity were greatly decreased by decreasing the ammonia concentration.

Oxidation of ammonia at low concentrations (1000 ppm NH_3 in He) was investigated at low tem-

Table 4
The dependence of the activity for ammonia oxidation of CuY (8.4 wt.%) catalysts on O_2/NH_3 feed ratio[a]

Catalyst	Temperature (°C)	O_2/NH_3 ratio	NH_3 conversion (%)	N_2 selectivity (%)
CuY (8.4 wt.%)	300	0.68	21	99.5
	300	2.60	46	99.0
	300	7.20	88	97
	400	0.68	94	98
	400	2.60	100	95.7
	400	7.20	100	86

[a] Flow rate=74.7 N ml/min; catalyst weight=0.2 g; $[NH_3]$=11 400 ppm.

Table 5
The effect of co-fed water vapor on the activity of copper-containing catalysts during ammonia oxidation[a]

Catalyst	Temperature (°C)	Feed	NH_3 conversion (%)	N_2 selectivity (%)
Cu/Al_2O_3 (10 wt.%)	300	Dry	90	96
	300	Wet	21	97
	350	Dry	100	94
	350	Wet	100	95
CuY (8.4 wt.%, NaOH treated)	250	Dry	56	97
	250	Wet	15	98
	300	Dry	100	98
	300	Wet	82	97
	350	Wet	100	98

[a] Reaction conditions: NH_3: 1.14 vol.%; O_2: 8.21 vol.%; H_2O: 5.2 vol.%; flow rate=74.7 N ml/min; catalyst weight=0.2 g.

Table 6
The activity of various catalysts for ammonia oxidation at low ammonia feed concentration (1000 ppm) in helium[a]

Catalyst	Temperature (°C)	NH_3 conversion (%)	N_2 selectivity (%)
Ir/Al_2O_3 (1.2 wt.%, reduced)	180	52	88
	200	100	84
Pt/Al_2O_3 (1.2 wt.%, reduced)	180	66	75
	200	100	75
Cu/Al_2O_3 (10 wt.%)	200	16	93
	230	66	86
	250	95	82
CuY (8.4 wt.%, with NaOH treatment)	200	36	92
	230	73	95
	250	100	94
CuY (8.4 wt.%, without NaOH treatment)	250	54	91
	300	100	85

[a] Reaction conditions: NH_3: 1000 ppm; O_2: 10 vol.%; O_2/NH_3=100; flow rate=50 N ml/min; catalyst weight=0.1 g.

Table 7
Activity of various catalysts for ammonia oxidation at high ammonia concentration (11 400 ppm NH_3 in helium)[a]

Catalyst	Temperature (°C)	NH_3 conversion (%)	N_2 selectivity (%)
CuY (8.4 wt.%, NaOH treated)	200	35	95
	250	63	97
Pt/Al_2O_3 (1.2 wt.%, reduced)	200	100	87
	190	33	82
Ir/Al_2O_3 (1.2 wt.%, reduced)	200	100	95
	165	32	92
Rh/Al_2O_3 (1.2 wt.%, reduced)	350	25	90
	400	100	86
Pd/Al_2O_3 (1.2 wt.%, reduced)	250	60	97
	300	100	98

[a] Reaction conditions: NH_3: 1.14 vol.%; O_2: 8.21 vol.%; O_2/NH_3=7.2; flow rate=74.7 N ml/min; catalyst weight=0.2 g.

peratures and the results are shown in Table 6. In all cases, the observed activity and selectivity of the catalysts decreased relative to those observed previously at higher concentrations. However, the selectivity observed on CuY catalysts at low concentrations still exceeded that obtained either on copper–alumina or on noble-metal catalysts under similar conditions. The measured activity of these catalysts at high NH_3 concentration (11 400 ppm NH_3 in He) is shown in Table 7 for comparison.

3.6. Comparison with the noble-metal catalysts

The results of Tables 6 and 7 show that noble-metal catalysts are very active even at low loading, however, their selectivity to nitrogen is very poor. By comparison, the copper-containing catalysts, especially CuY catalysts, are more promising. These catalysts may be applied at temperatures below 300°C and possess higher activity and selectivity compared with noble-metals.

4. Conclusions

The activity of copper ion-exchanged zeolite Y catalysts for ammonia oxidation was shown to be comparable to that of noble-metal catalysts at low temperatures. The selectivity to nitrogen was much higher for the zeolite catalysts. Treatment of CuY with NaOH after ion exchange increased the ammonia oxidation activity. This effect is probably due to the change in particle size and dispersion of the copper oxide on the support. Co-fed steam dramatically decreased catalyst activity, especially at lower temperatures. Ion-exchanged zeolite Y catalysts were more stable than alumina-supported catalysts. At high O_2/NH_3 ratio the activity of all catalysts increased but the selectivity for nitrogen production decreased.

References

[1] M. Amblard, R. Burch, B.W.L. Southward, Appl. Catal. B 22 (3) (1999) L159.
[2] J.J.P. Biermann, Ph.D. Thesis, University of Twente, Twente, 1990.
[3] N.I. Il’chenko, Russ. Chem. Rev. 45 (12) (1976) 1119.
[4] J.J. Ostermaier, J.R. Katzer, W.H. Manogue, J. Catal. 41 (1976) 277.
[5] J.J. Ostermaier, J.R. Katzer, W.H. Manogue, J. Catal. 33 (1974) 457.
[6] J.E. Delaney, W.H. Manogue, in: Proceedings of the Fifth International Congress on Catalysis, Vol. 1, 1973, p. 267.
[7] O.V. Al’tshuller, M.Ya. Kushnerev, Problemy Kinetiki I Kataliza 15 (1973) 56.
[8] N.N. Sazonova, A.V. Simakov, H. Veringa, React. Kinet. Catal. Lett. 57 (1) (1996) 71.
[9] F.J.J.G. Janssen, F.M.G. van den Kerkhof, Selective catalytic removal of NO from stationary sources, KEMA Science and Technical Reports, Vol. 3, 1985, p. 6.
[10] J.P. Chen, R.T. Yang, Appl. Catal. 80 (1992) 135.
[11] G. Tuenter, W.F. van Leeuwen, L.J.M. Snepvangers, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 633.
[12] E.T.C. Vogt, A. Boot, J.W. Geus, F.J.J.G. Janssen, J. Catal. 114 (1988) 313.
[13] E.T.C. Vogt, Ph.D. Thesis, University of Utrecht, Utrecht, 1988.
[14] J.J.P. Biermann, F.J.J.G. Janssen, J.W. Geus, J. Mol. Catal. 60 (1990) 229.
[15] M. de Boer, A.J. van Dillen, J.W. Geus, Catal. Lett. 11 (1991) 227.
[16] Y. Li, J.N. Armor, Appl. Catal. B 13 (1997) 131.
[17] A. Wollner, F. Lange, Appl. Catal. A 94 (1993) 181.
[18] K.G. Ione, P.N. Kuznetsov, V.N. Romannikov, Application of Zeolite in Catalysis, Vol. 87, Akadémi Kiadò, Budapest, 1979.
[19] R.A. Schoonheydt, K.G. Ione, P.N. Kuznetsov, V.N. Romannikov, J. Catal. 43 (1976) 292.
[20] M. Suzuki, K. Tsutsumi, H. Takahashi, Y. Saito, Zeolites 8 (1988) 284.
[21] M. Suzuki, K. Tsutsumi, H. Takahashi, Y. Saito, Zeolites 8 (1988) 387.
[22] N. Watanabe, H. Yamashita, H. Miyadera, S. Tominaga, Appl. Catal. B 8 (1996) 405.
[23] S.E. Golunski, H.A. Hatcher, R.R. Rajaram, T.J. Truex, Appl. Catal. B 5 (1995) 367.
[24] G. Lu, J. van Grondelle, B.G. Anderson, R.A. van Santen, J. Catal. 186 (1999) 100.