

Selective catalytic oxidation of ammonia from MAP decomposition

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Abstract

The Cu/TiO₂ catalysts with different Cu loadings were prepared, and their performance in the selective catalytic oxidation of ammonia (SCO of NH₃) was compared with 10% Cu/Al₂O₃. The 10% Cu/TiO₂ has the best performance among its series for NH₃ conversion and N₂ selectivity. At 250 °C, the 100% conversion of ammonia was achieved and the selectivity to N₂ came to 95%. The 10% Cu/TiO₂ catalyst has a much higher activity for the SCO of ammonia and a slightly lower N₂ selectivity than 10% Cu/Al₂O₃ because of the higher oxygen mobility and lower oxygen bonding strength, which demonstrated that TiO₂ is a more suitable support than Al₂O₃ for copper-based catalyst in the SCO of NH₃. The mechanisms involved in the SCO of NH₃ reaction on the 10% Cu/TiO₂ catalyst have also been investigated using TPD, TPR as well as in situ DRIFTS methods. © 2007 Elsevier B.V. All rights reserved.

Keywords: Selective catalytic oxidation of ammonia; Copper; Titania; Alumina; In situ DRIFTS

1. Introduction

Formation of magnesium ammonium phosphate (MAP) has been considered to be an effective method for the removal of ammonium from landfill leachate because of its high reaction rate and low residual ammonium concentration [1–3]. However, the high operating cost, due to the continual addition of fresh phosphate and magnesium, is the main obstacle to widespread application of the MAP process. This problem can be effectively solved by repeated use of the MAP decomposition residues formed at the conditions of NH₄⁺:OH⁻ molar ratio, 1:1; temperature, 90 °C; heating time, 2 h, and the chemical costs can be saved for about 50% by reuse of MAP for 3 cycles [4]. The high ammonia emission in the process of MAP decomposition, however, should be controlled properly to prevent serious air pollution.

Among the methods to abate ammonia emission, low temperature selective catalytic oxidation (SCO) of ammonia to nitrogen is potentially seen as an ideal technology [5,6]. Previous studies show that noble metals such as Pt is active for this reaction at low temperature but deactivate rapidly with time [7]. Silver based catalysts have a high activity for ammonia conversion, but the N₂ selectivity is relatively low at the temperature range investigated [8]. Al₂O₃-supported metal oxide catalysts such as Cr₃O₄,

Fe₂O₃, CuO and MoO₃ have been widely studied, but ammonia conversion levels are not high enough at low temperatures to be of practical use [9–12].

In our previous study, we found that alumina supported copper-silver catalyst had a good conversion and selectivity to N₂, and the complete ammonia conversion could be achieved at 320 °C [13]. However, the conversion temperature is still too high for the oxidation of ammonia produced during MAP decomposition. Sazonova et al. [14] had reported that the Cu/TiO₂ catalyst possessed a good activity for the SCO of ammonia to N₂ at the temperature around 300 °C. However, the reaction mechanism, limitative conditions and characterization of this catalyst were not detailed in this report.

In this study, we prepared Cu/TiO₂ catalysts with different Cu loadings, and evaluated the activity of Cu/TiO₂ catalysts for the SCO of ammonia to N₂ in detail. X-ray diffraction analysis (XRD), temperature programmed desorption (TPD) and reduction (TPR) as well as in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were used for a better understanding of the SCO of ammonia on Cu/TiO₂ catalyst.

2. Experimental

2.1. Catalyst preparation

The TiO₂ and Al₂O₃ supported copper catalysts were prepared by an impregnation method with an anatase type TiO₂ (Shanghai, China) and an aqueous solution of Cu(NO₃)₂. After

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impregnation, the excessive water was removed in a rotary evaporator at 80 °C. The samples were dried at 110 °C for 12 h and then calcined at 450 °C for 3 h.

2.2. Activity test of catalyst

The activity tests for the SCO of NH₃ over catalysts were performed with a fixed-bed quartz flow reactor by passing a gas mixture of NH₃/O₂/He = 400 ppm/10 vol%/balance at a total flow rate of 500 cm³ min⁻¹ (gas hourly space velocities (GHSV): 50,000 h⁻¹). Ammonia, oxygen and helium flow rates were controlled by mass flow controllers. Water was supplied with a micro-pump into the gas stream and vaporized by a coiled heater at the inlet of the reactor. The inlet and outlet gas compositions were analyzed by an on-line NEXUS 670-FTIR fitted with a gas cell of volume 2 dm³.

2.3. Characterization of catalyst

BET surface areas were obtained from N₂ adsorption isotherms measured at 77 K using an ASAP 2000 instrument (Micromeritics Co. USA). Powder X-ray diffraction (XRD) measurements of catalysts were carried out on a Rigaku D/max-RB X-ray diffractometer (Japan) with a Cu K α radiation and operated at 40 kV and 40 mA. The patterns were taken in the 2 θ range of 10–70° at a scan speed of 6° min⁻¹.

NH₃-TPD or TPR experiments were performed using a fixed-bed flow reactor system equipped with a computer-interfaced quadruple mass spectrometer (Hiden HPR 20). After adsorption of NH₃ at room temperature the TPD or TPR data were recorded by mass spectrometer while the temperature was increased from 50 to 500 °C at a heating rate of 20 °C/min.

2.4. In situ DRIFTS

In situ DRIFT spectra were recorded in a NEXUS 670-FTIR equipped with a smart collector and a liquid N₂ cooled MCT detector. The sample (about 30 mg) for study was finely grounded and placed in a ceramic crucible. A flow of feed gas mixture was controlled by mass flow meters. All spectra were recorded with a resolution of 4 cm⁻¹ and accumulating 100 scans. The background spectrum was subtracted from each spectrum, respectively.

3. Results and discussion

3.1. Catalytic test

3.1.1. Ammonia oxidation on copper-based catalysts

The NH₃ conversion performance of Cu/TiO₂ catalysts with different Cu loadings was compared with that of 10% Cu/Al₂O₃ (weight percent, hereinafter) at various temperatures, and the results are shown in Figs. 1 and 2. The NH₃ conversion increased significantly with the increase of copper loading from 1 to 10%, and then remained almost unchanged with the further increase of copper loading from 10 to 20%. It is clear that activity of 10%Cu/TiO₂ for the NH₃ conversion was far higher than that

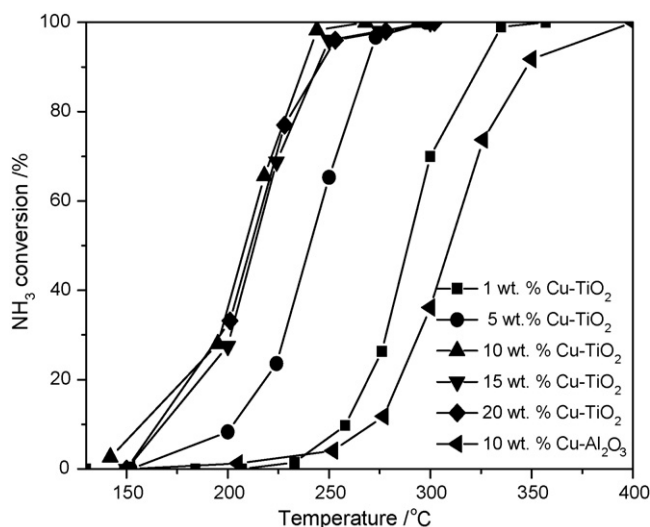


Fig. 1. NH₃ conversion during the SCO of NH₃ over Cu/TiO₂ with different Cu loadings and 10% Cu/Al₂O₃ catalysts. Reaction conditions: 0.2 g catalyst, [NH₃] = 400 ppm, [O₂] = 10%, He = balance, total flow rate = 500 ml min⁻¹ and GHSV = 50,000 h⁻¹.

of 10% Cu/Al₂O₃ (100% ammonia conversion was achieved at about 350 °C), which was developed in the previous study [15]. The selectivity of NH₃ to N₂, on the other hand, decreased with the increase of copper content. Chmielarz et al. [16] found that the increase of copper loading favors the formation of surface metal oxide clusters and decreases the oxygen bonding strength, leading to the decrease of N₂ selectivity of Cu/Mg/Al catalysts. Therefore, considering NH₃ conversion and N₂ selectivity, the 10% Cu/TiO₂ is the best one among its series catalysts, over which complete conversion of NH₃ and an N₂ selectivity of 95% were obtained at 250 °C. In comparison with the 10% Cu/Al₂O₃ catalyst, the 10% Cu/TiO₂ catalyst demonstrated a similar N₂ selectivity but a much high catalytic activity for ammonia oxidation. This indicates that TiO₂ is a more suitable support than Al₂O₃ for copper-based catalyst in the SCO of NH₃.

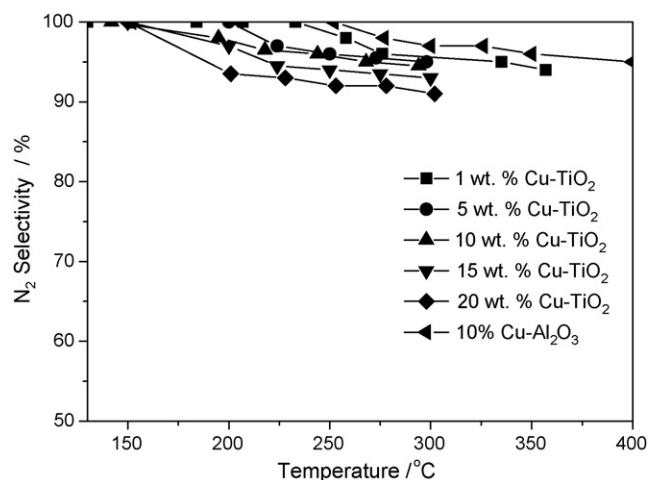


Fig. 2. N₂ selectivity during the SCO of NH₃ over Cu/TiO₂ with different Cu loadings and 10% Cu/Al₂O₃ catalysts. Reaction conditions: 0.2 g catalyst, [NH₃] = 400 ppm, [O₂] = 10%, He = balance, total flow rate = 500 ml min⁻¹ and GHSV = 50,000 h⁻¹.

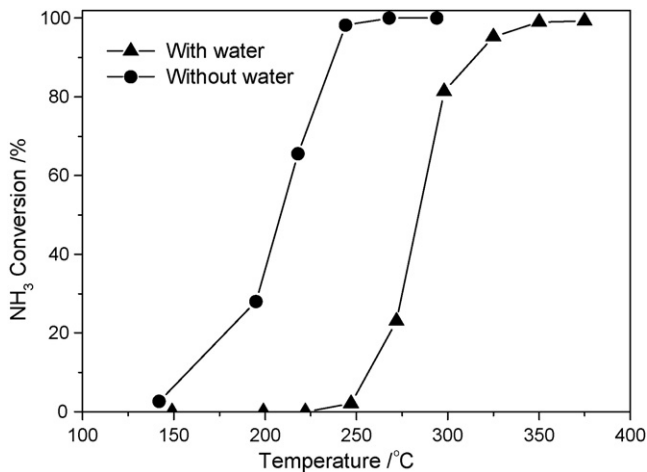


Fig. 3. Effect of H₂O on NH₃ conversion for 10% Cu/TiO₂ catalyst. Reaction conditions: 0.2 g catalyst, [NH₃] = 400 ppm, [O₂] = 10%, 3% water vapor, He = balance, total flow rate = 500 ml min⁻¹ and GHSV = 50,000 h⁻¹.

3.1.2. Effect of water on catalytic activity

It is known that waste streams sometimes contain water vapour, so the effect of water on the catalytic performance of the 10% Cu/TiO₂ was investigated. As shown in Fig. 3, the temperature for complete NH₃ conversion increased for about 100 °C when 3% H₂O existed in the waste stream, indicating the existence of adverse effects by water composition. It is likely that water competes with ammonia for the absorption sites [17]. As shown in Fig. 4, the N₂ selectivity was hardly influenced by the existence of water in the waste stream. Therefore, it is important that the content of water should be checked in utilizing the catalyst for the removal of NH₃.

3.2. XRD and BET results

Fig. 5 shows the XRD patterns of Cu/TiO₂ catalysts with different Cu loadings. All the catalysts exhibited the typical patterns of anatase TiO₂, and the XRD intensity of TiO₂ did not change with the changes of Cu loading. Perceptible XRD pat-

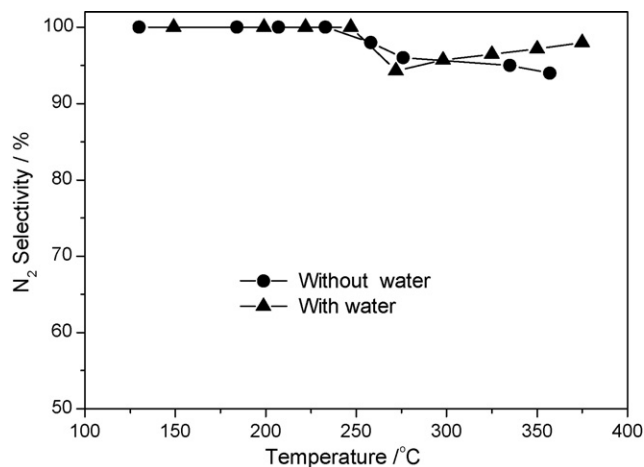


Fig. 4. Effect of H₂O on N₂ selectivity for 10% Cu/TiO₂ catalyst. Reaction conditions: 0.2 g catalyst, [NH₃] = 400 ppm, [O₂] = 10%, 3% water vapor, He = balance, total flow rate = 500 ml min⁻¹ and GHSV = 50,000 h⁻¹.

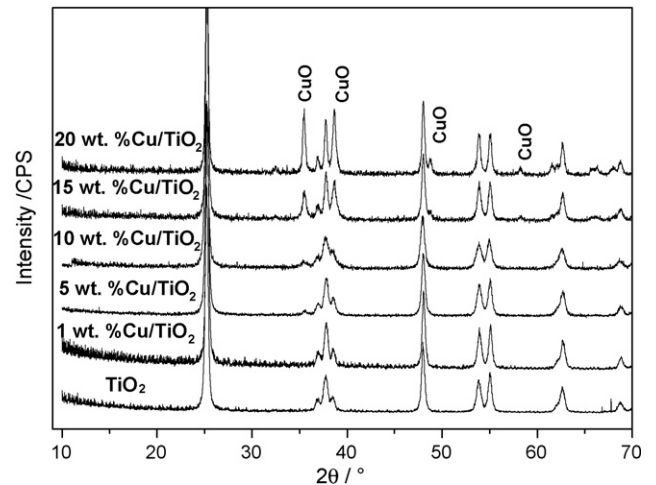


Fig. 5. XRD patterns of Cu/TiO₂ catalysts with different Cu loadings.

tern (35.5, 38.6, 48.9 and 58.3) attributable to crystallized CuO was observed with the loading of Cu increased. It means that the particles of CuO well dispersed on the surface of TiO₂ at low copper loadings, and the increase of copper loading caused the aggregation of CuO on the TiO₂ surface. As shown in Fig. 6, the XRD spectrum of 10% Cu/TiO₂ only exhibited very weak diffractive pattern attributable to crystallized CuO, and the XRD spectrum of 10% Cu/Al₂O₃ did not show any CuO pattern. This indicates that particle size of CuO deposited on TiO₂ is larger than that on Al₂O₃, and the CuO phase is much higher dispersed on Al₂O₃ than TiO₂. Combining the XRD results with the results in Figs. 1 and 2, it is indicated that the N₂ selectivity related with CuO particle size [16].

BET surface areas of Cu/TiO₂ catalysts with different Cu loadings are shown in Table 1 together with that of 10% Cu/Al₂O₃. Table 1 shows that the loading of copper did not affect the structure of TiO₂ except for the case of 20% Cu/TiO₂. Compared with 10% Cu/TiO₂, 10% Cu/Al₂O₃ has a much higher surface area, which may be the reason that the dispersion of CuO on 10% Cu/Al₂O₃ was better than that of 10% Cu/TiO₂. These results also indicate that BET surface area was not the

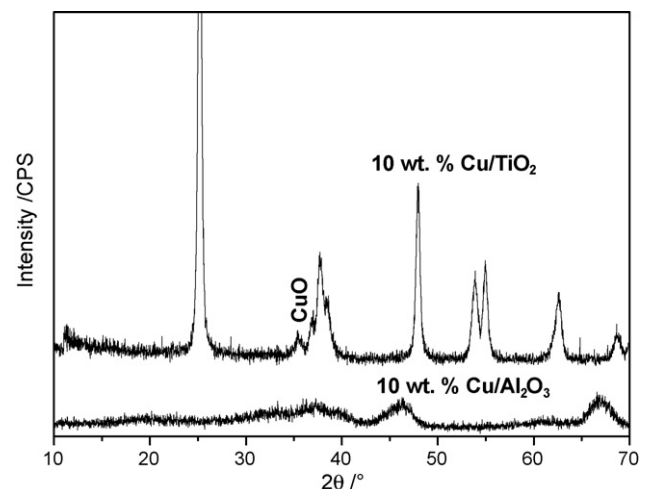


Fig. 6. XRD patterns of 10% Cu/TiO₂ and 10% Cu/Al₂O₃ catalysts.

Table 1
BET surface areas of Cu/TiO₂ catalysts with different Cu loadings and 10% Cu/Al₂O₃

Sample	BET surface area (m ² /g)
TiO ₂	119.8
1 wt.% Cu/TiO ₂	112.3
5 wt.% Cu/TiO ₂	124.6
10 wt.% Cu/TiO ₂	122.8
15 wt.% Cu/TiO ₂	108.8
20 wt.% Cu/TiO ₂	82.7
10 wt.% Cu/Al ₂ O ₃	171.9

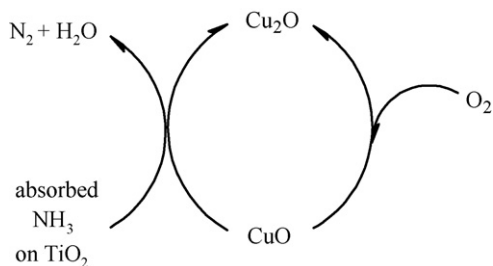


Fig. 7. Schematic mechanism of the SCO of NH₃ on Cu/TiO₂.

main factor for the great difference of the activity between the two catalysts, and the synergetic effect between active CuO and the support might play an important role. We supposed that the SCO of ammonia on Cu/TiO₂ followed the oxidation–reduction mechanism shown in Fig. 7. Free ammonia was firstly adsorbed on the surface of TiO₂, and then the adsorbed ammonia was oxidized through the redox cycle of CuO and Cu₂O at certain temperature. Therefore, the catalytic activity of Cu/TiO₂ should be closely related to the NH₃ adsorption on support and the redox ability of active component.

3.3. TPR of ammonia

The strength of oxygen bonding in 10% Cu/TiO₂ and 10% Cu/Al₂O₃ was determined by the TPR method. The TPR profiles of ammonia are shown in Fig. 8a and b, respectively. Forma-

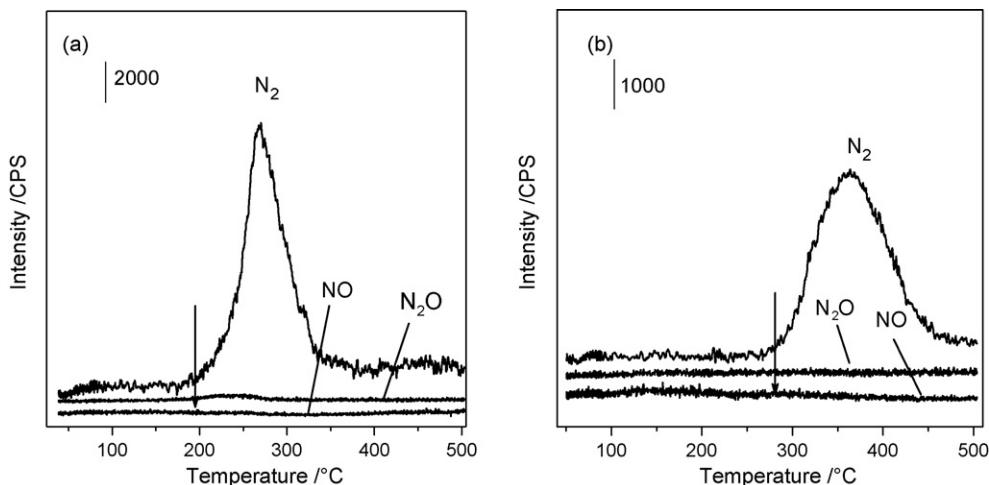


Fig. 8. Ammonia TPR profile on the catalysts of 10 wt.% Cu/TiO₂ (a) and 10 wt.% Cu/Al₂O₃ (b).

tion of N₂ on the 10% Cu/TiO₂ starts at temperature 200 °C and reaches the maximum at about 250 °C, while that on the Cu/Al₂O₃ starts from 275 °C, and reaches the maximum at 370 °C. These results indicate that reduction of CuO on TiO₂ is easier than that on Al₂O₃ by NH₃. The oxygen mobility on 10% Cu/TiO₂ is higher than that on Cu/Al₂O₃, which is probably responsible for the much higher SCO activity of Cu/TiO₂ than that of Cu/Al₂O₃ [16]. Apart from nitrogen production, trace amount of N₂O was also produced on the Cu/TiO₂ during the NH₃-TPR, but no NO_x was detected, even at higher temperature.

3.4. TPD of adsorbed ammonia

The surface acidity of the catalysts was measured by TPD of ammonia (NH₃-TPD), and the TPD profiles of ammonia on 10% Cu/TiO₂ and Cu/Al₂O₃ are shown in Fig. 9. NH₃ desorption occurs from room temperatures up to 350 °C. Three peaks of ammonia desorption appeared, indicating that three major ammonia species differing in thermal stability exist on catalyst surface. The first two peaks should correspond to the physical desorption, and the last peak should be attributable to the chemical desorption. N₂ and trace amount of N₂O were also found around 270 °C from the reaction of chemisorbed NH₃. However, no formation of NO was observed within the investigated temperatures. As shown in Fig. 9b, the 10% Cu/Al₂O₃ catalyst has a similar TPD profile of ammonia to 10% Cu/TiO₂. The desorption peaks of ammonia, N₂ and trace amount of N₂O were observed, whereas NO desorption was not detected. The difference is that the chemical desorption occurred at different temperatures: 250 °C for 10% Cu/TiO₂, and 350 °C for 10% Cu/Al₂O₃, which is consistent with the experimental results of Gutiérrez–Alejandro's study that the temperature of ammonia chemical desorption decreased when the alumina support was mixed with titania [18]. It should be noted that no major change was observed when ammonia was co-adsorbed with oxygen.

3.5. DRIFT results

Fig. 10 shows the in situ DRIFT spectra of 10% Cu/TiO₂ in a flow of NH₃ + O₂ at various temperatures. The bands found

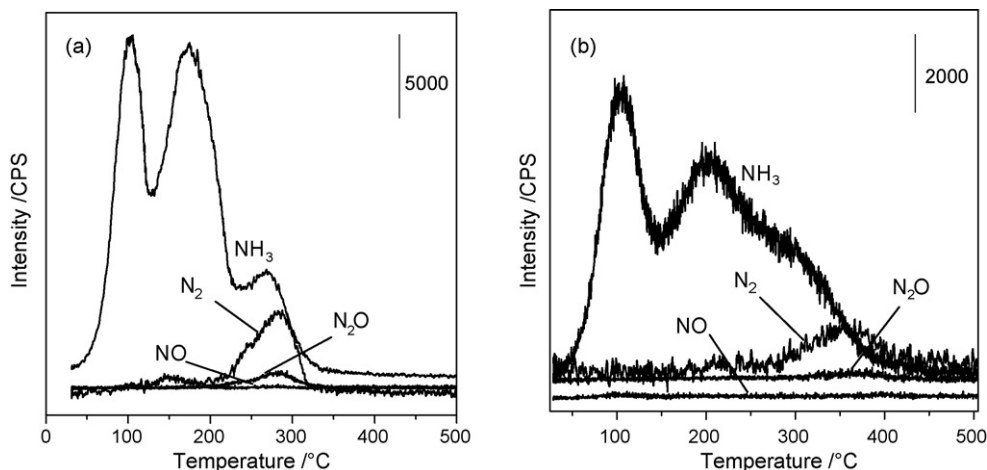
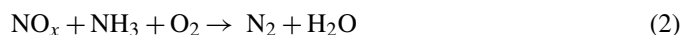


Fig. 9. Ammonia TPD profile on the catalysts of 10% Cu/TiO₂ (a) and 10 wt.% Cu/Al₂O₃ (b).

at 1608 and 1223 cm⁻¹ can be assigned to the asymmetric and symmetric deformation modes of ammonia, respectively, coordinated on Lewis acid sites. The bands at 3390, 3356, 3250 and 3149 cm⁻¹ could be assigned to the N–H stretching modes [19]. The bands at 1699 and 1460 cm⁻¹ were due to the asymmetric and symmetric deformation modes of ammonia coordinated on Bronsted acid sites. The band at 1365 cm⁻¹ can be assigned to –NH₂ wagging deformation modes [20]. The intensities of these bands gradually decrease with the increasing of sample temperature. Compared with the TPD of NH₃ (Fig. 9), the desorption of unreacted NH₃ and the activation of NH₃ are responsible for these decreases. In addition, it was worthy of note that no nitrate species appear over the temperature range investigated.

For the route of the SCO of ammonia to N₂, two pathways have been proposed in the literature. The first is the in situ

“internal” selective catalytic reduction (iSCR). It is a two-step mechanism involving the oxidation of a significant percentage of the NH₃ into NO_x species as follows [6]:



The second is a direct route based on the recombination of 2NH_x species giving rise to a hydrazinium intermediate H_xN–NH_x [20,21], and the reactions are as follows:

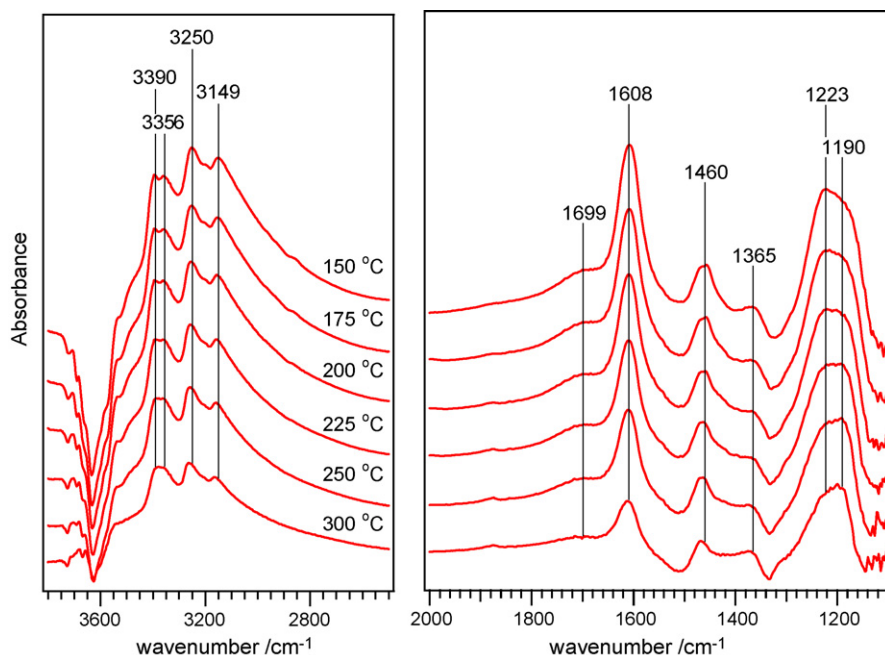
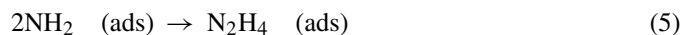
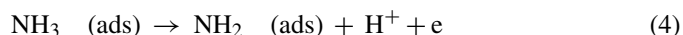
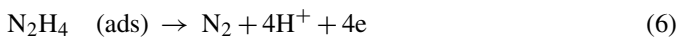


Fig. 10. In situ DRIFT spectra of 10% Cu/TiO₂ catalyst in a flow of NH₃ + O₂ at various temperatures. Reaction conditions: 0.2 g catalyst, [NH₃] = 400 ppm, [O₂] = 10%, He = balance, total flow rate = 500 ml min⁻¹ and GHSV = 50,000 h⁻¹.



According to our results of TPR, TPD and DRIFTS of Cu/TiO₂, the first hypothesis was apparently ruled out, because there did not appear NO_x species in the experimental process. Therefore, the direct path way was suitable for the SCO of ammonia to N₂ on Cu/TiO₂ catalyst, i.e., the oxidation of NH_x species directly to atomic nitrogen and then the recombination of two nitrogen atoms forming N₂, or the recombination of NH_x species giving rise to an hydrazinium intermediate N₂H₄ and then oxidizing to N₂.

4. Conclusions

The TiO₂ supported copper catalyst was found to be active for ammonia oxidation. The Cu/TiO₂ with 10% Cu loading shows the best performance in its series in terms of NH₃ conversion and N₂ selectivity. Compared with Al₂O₃, TiO₂ demonstrate a much higher activity for the SCO of ammonia as the supporting material because of the higher oxygen mobility in the system. The results of TPR, TPD and DRIFTS show that the SCO of NH₃ follows the direct route, not the two-step mechanism.

Acknowledgements

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References

- [1] X.Z. Li, Q.L. Zhao, X.D. Hao, Ammonium removal from landfill leachate by chemical precipitation, *Waste Manage.* 19 (1999) 409–415.
- [2] M. Altinbas, C. Yangin, I. Ozturk, Struvite precipitation from anaerobically treated municipal and landfill wastewaters, *Water Sci. Technol.* 46 (2002) 271–278.
- [3] I. Stratful, M.D. Scrimshaw, J.N. Lester, Conditions influencing the precipitation of magnesium ammonium phosphate, *Water Res.* 35 (2001) 4191–4199.
- [4] S. He, Y. Zhang, M. Yang, W. Du, H. Harada, Repeated use of MAP decomposition residues for the removal of high ammonium concentration from landfill leachate, *Chemosphere* 66 (2007) 2233–2238.
- [5] M. Amblard, R. Burch, B.W.L. Southward, Study of the mechanism of selective conversion of ammonia to nitrogen on Ni/γ-Al₂O₃ under strongly oxidizing conditions, *Catal. Today* 59 (2000) 365–371.
- [6] M. de Boer, H.M. Huisman, R.J.M. Mos, R.G. Leliveld, A.J. Dillen, J.W. Geus, Selective oxidation of ammonia to nitrogen over SiO₂-supported MoO₃ catalysts, *Catal. Today* 17 (1993) 189–200.
- [7] J.J. Ostermaier, J.R. Katzer, W.H. Manogue, Crystallite size effects in the low-temperature oxidation of ammonia over supported platinum, *J. Catal.* 33 (1974) 457–473.
- [8] G. Lu, B.G. Anderson, J. van Grondelle, R.A. van Santen, Low temperature selective oxidation of ammonia to nitrogen on silver-based catalysts, *Appl. Catal. B* 40 (2003) 101–110.
- [9] F.J.J.G. Janssen, F.M.G. Kerkhof, Selective catalytic removal of NO from stationary sources, *KEMA Sci. Technol. Rep.* 3 (1985).
- [10] E.T.C. Vogt, A. Boot, J.W. Geus, F.J.J.G. Janssen, Preparation and performance of a silica-supported V₂O₅ on TiO₂ catalyst for the selective reduction of NO with NH₃, *J. Catal.* 114 (1988) 313–320.
- [11] G. Tuenter, W.F. van Leeuwen, L.J.M. Snepvangers, Kinetics and mechanism of the NO_x reduction with NH₃ on V₂O₅-WO₃-TiO₂ catalyst, *Ind. Eng. Chem. Prod. Res. Dev.* 25 (1986) 633–636.
- [12] J.J.P. Biermann, F.J.J.G. Janssen, J.W. Geus, Molybdena on silica catalysts: selective catalytic oxidation of ammonia to nitrogen over MoO₃ on SiO₂ catalysts, *J. Mol. Catal.* 60 (1990) 229–238.
- [13] M. Yang, C. Wu, C. Zhang, H. He, Selective oxidation of ammonia over copper-silver-based catalysts, *Catal. Today* 90 (2004) 263–267.
- [14] N.N. Sazonova, A.V. Simakov, T.A. Nikoro, G.B. Barannik, V.F. Lyakhova, V.I. Zheivot, Z.R. Ismagilov, H. Veringa, Selective catalytic oxidation of ammonia to nitrogen, *React. Kinet. Catal. Lett.* 57 (1996) 71–79.
- [15] J. Lu Gang, B.G. van Grondelle, R.A. Anderson, van Santen, Selective low temperature NH₃ oxidation to N₂ on copper-based catalysts, *J. Catal.* 186 (1999) 100–109.
- [16] L. Chmielarz, P. Kustrowski, A. Rafalska-Lasocha, R. Dziembaj, Selective oxidation of ammonia to nitrogen on transition metal containing mixed metal oxides, *Appl. Catal. B* 58 (2005) 235–244.
- [17] Y. Li, J.N. Armor, Selective NH₃ oxidation to N₂ in a wet stream, *Appl. Catal. B* 13 (1997) 131–139.
- [18] A. Gutiérrez-Alejandre, M. González-Cruz, M. Trombetta, G. Busca, J. Ramírez, Characterization of alumina–titania mixed oxide supports: Part II: Al₂O₃-based supports, *Microporous Mesoporous Mater.* 23 (1998) 265–275.
- [19] G. Ramis, L. Yi, G. Busca, M. Turco, E. Kotur, R.J. Willey, Adsorption, activation, and oxidation of ammonia over SCR catalysts, *J. Catal.* 157 (1995) 523–535.
- [20] G. Ramis, L. Yi, G. Busca, Ammonia activation over catalysts for the selective catalytic reduction of NO_x and the selective catalytic oxidation of NH₃: an FT-IR study, *Catal. Today* 28 (1996) 373–380.
- [21] J.M.G. Amores, V.S. Escribano, G. Ramis, G. Busca, An FT-IR study of ammonia adsorption and oxidation over anatase-supported metal oxides, *Appl. Catal. B* 13 (1997) 45–58.