

Selective oxidation of ammonia over copper-silver-based catalysts

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Abstract

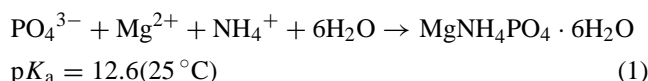
A novel catalyst based on copper-silver was developed to solve the contradiction between the high conversion temperature of Cu-based catalyst and low N₂ selectivity of Ag-based catalyst during selective oxidation of ammonium gas. The Cu-Ag-based catalyst (Cu 5 wt.-%-Ag 5 wt.-%/Al₂O₃) displayed a relatively low complete conversion temperature (<320 °C) with a high N₂ selectivity (>95%). Increasing loading of Cu and Ag decreases N₂ selectivity. The low N₂ selectivity of Ag-based catalyst is possibly related to the formation of Ag₂O crystals. Improvement of N₂ selectivity of Ag-based catalyst was obtained by doping Cu to decrease crystallized Ag₂O phase. The temperature programmed reaction (TPR) data show that N₂O is the main byproduct of oxidation of ammonia at temperature lower than 200 °C. Two bands of nitrate species at 1541 and 1302 cm⁻¹ were observed on Ag 10 wt.-%/Al₂O₃ at the temperature higher than 250 °C, which indicates the formation of NO_x during the selective catalytic oxidation of ammonia. No nitrate species was observed on Cu 10 wt.-%/Al₂O₃ and Cu 5 wt.-%-Ag 5 wt.-%/Al₂O₃, while only one nitrate species (1543 cm⁻¹) existed on Cu 10 wt.-%-Ag 10 wt.-%/Al₂O₃. We proposed that mixing Ag with Cu inhibited the formation of NO_x during the selective catalytic oxidation of ammonia over Cu-Ag/Al₂O₃.

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1. Introduction

Ammonium removal from landfill leachate has long been a big challenge. Biological processes, which have been widely utilized for ammonium removal from municipal wastewater and industrial wastewater, are not a proper candidate for treating landfill leachate because of high ammonium concentration (10²–10³ mg/l) and lack of sufficient electron donors for biological denitrification. Magnesium ammonium phosphate (MAP) precipitation as shown in Eq. (1), on the other hand, has been considered to be an effective method for solving the ammonium removal problems because of its high reaction rate and no requirement for electron donors [1–3]. However, the running cost will be very high if MAP is thrown away without recovering its magnesium and phosphate components



on the other hand, MAP will be decomposed into ammonium gas and MgHPO₄ when it is heated to a certain temperature with the reasonable temperature of about 300 °C. MgHPO₄ could be utilized for ammonium removal again instead of fresh magnesium and phosphate chemicals. However, high concentration ammonia emission will become a problem for reuse of MAP. Selective oxidation of NH₃ to N₂ has been studied for different purposes [4–6]. A lot of catalysts, including γ-Al₂O₃-supported Ni, Fe, Mn, Cu and Ag, have been utilized for the selective oxidation of NH₃. NH₃ could be converted to N₂ on a copper-based catalyst supported on zeolite Y at 350 °C with the N₂ selectivity as high as 98% [6]. Silver-based catalysts supported on Al₂O₃ demonstrated a much lower conversion temperature (<200 °C). However, the high activity was acquired at the expense of low N₂ selectivity (82% or lower) [7].

In this study, a novel catalyst based on copper-silver was developed to solve the contradiction between conversion temperature and N₂ selectivity on using single metal catalysts. Two kinds of catalysts, i.e., Cu 5 wt.-%-Ag 5 wt.-%/Al₂O₃ and Cu 10 wt.-%-Ag 10 wt.-%/Al₂O₃, were proposed, and their respective activity and selectivity were compared with the single metal catalysts. Structural infor-

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mation of the new catalysts was acquired using instruments like X-ray diffraction (XRD) and Fourier transform infrared reflectance (FTIR).

2. Experimental

2.1. Catalyst preparation

Four kinds of catalysts, i.e., Cu 10 wt.%/Al₂O₃, Cu 5 wt.%-Ag 5 wt.%/Al₂O₃, Cu 10 wt.%-Ag 10 wt.%/Al₂O₃, Ag 10 wt.%/Al₂O₃, were respectively prepared by incipient wetness impregnation of Al₂O₃ (gamma type, BET 250 m²/g) with solution of Cu(NO₃)₂, Cu(NO₃)₂-AgNO₃, or AgNO₃, followed by evaporation to dryness in a rotary evaporator under pressure reduction at 60 °C. The wet sample was dried at 120 °C for 12 h, and then calcined in air at 600 °C for 3 h. Before the catalytic test, the catalysts were sieved into 20–40 meshes.

2.2. Catalyst testing

Catalytic activity measurements were carried out in a quartz fixed-bed reactor (15 mm internal diameter). 0.8 g of samples was used for each batch. NH₃, O₂, and He were mixed in a volume ratio of 1:10:89 before entering the reactor. The flow rates of NH₃, O₂, and He were controlled by mass flow controllers. The outlet gas was first analysed by Gas Chromatograph for N₂, and then washed with acid solution to trap NH₃ in the acid solution and ammonium nitrogen was analysed according to Standard Methods for the Examination of Water and Wastewater (APHA, 1985). The TPR was performed on a typical computer-controlled temperature programmed reduction apparatus. The temperature was ramped from 50 to 400 °C at a rate of 15 °C/min. Fragmentation patterns of NH₃ (*m/e* = 17), N₂ (*m/e* = 28), N₂/O (*m/e* = 44), NO (*m/e* = 30) and NO₂ (*m/e* = 46) were determined.

2.3. Catalyst characterization

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were recorded in a NEXUS 670-FTIR (4 cm⁻¹ resolution) equipped with a smart collector and a liquid N₂ cooled MCT detector. The sample (about 30 mg) for study was placed in a ceramic crucible. Before the experiment, the catalyst was firstly pre-treated in a flow of 30% O₂ and 70% N₂ for 60 min at 500 °C, then cooled down to a suitable temperature in a flow of O₂ and N₂ for 15 min and a spectrum of the catalyst in the flow of N₂ and O₂ served as the background was recorded. A flow of feed gas mixture controlled by mass flow meters was fed at a flow rate of 100 N ml/min. All spectra were measured under real reaction conditions with a resolution of 4 cm⁻¹ and accumulating 100 scans.

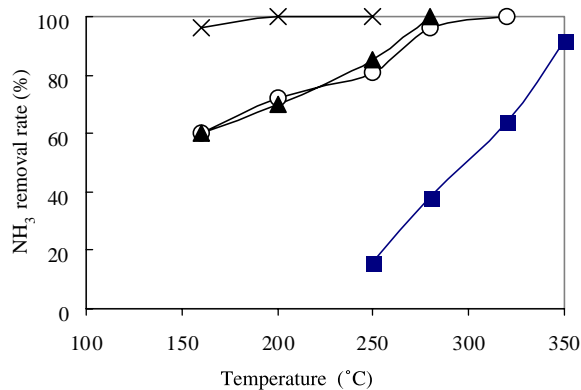


Fig. 1. NH₃ oxidation on catalysts. Reaction conditions: NH₃ 1%; O₂ 10%; He 89%; total flow rate, 400N ml/min; catalyst weight, 0.8 g. (■) Cu 10 wt.%/Al₂O₃, (○) Cu 5 wt.%-Ag 5 wt.%/Al₂O₃, (▲) Cu 10 wt.%-Ag 10 wt.%/Al₂O₃, (×) Ag 10 wt.%/Al₂O₃.

3. Results and discussion

3.1. NH₃ conversion performance

Figs. 1 and 2 shows the NH₃ conversion performance of Cu 10 wt.%/Al₂O₃, Cu 5 wt.%-Ag 5 wt.%/Al₂O₃, Cu 10 wt.%-Ag 10 wt.%/Al₂O₃ and Ag 10 wt.%/Al₂O₃ under different temperatures. The Cu 10 wt.%/Al₂O₃ presents high N₂ selectivity under different temperatures but has lower oxidation activity under the temperature lower than 350 °C. The Ag 10 wt.%/Al₂O₃ has high oxidation activity under a low temperature of 200 °C but the N₂ selectivity is lower. It indicates that the Ag-based catalyst (Ag 10 wt.%/Al₂O₃) had a higher activity for NH₃ conversion while the Cu-based catalyst (Cu 10 wt.%/Al₂O₃) had a higher N₂ selectivity, which is in accordance with the results of other researchers [6,7]. The Cu 5 wt.%-Ag 5 wt.%/Al₂O₃ catalyst, however, displayed a much lower complete conversion temperature (<320 °C) with a high N₂ selectivity (>95%). It is clear that proper mixing of the two metals could produce the catalyst

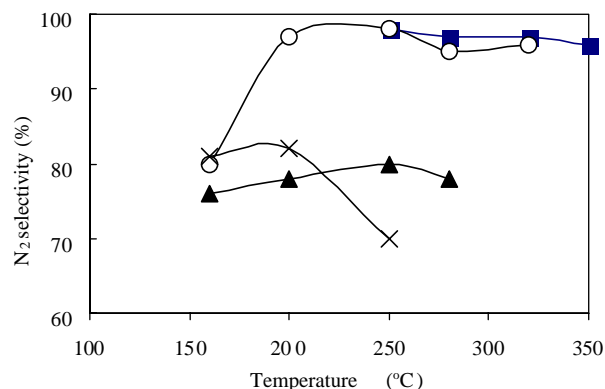


Fig. 2. N₂ selectivity of different catalysts. Reaction conditions: NH₃ 1%; O₂ 10%; He 89%; total flow rate, 400N ml/min; catalyst weight, 0.8 g. (■) Cu 10 wt.%/Al₂O₃, (○) Cu 5 wt.%-Ag 5 wt.%/Al₂O₃, (▲) Cu 10 wt.%-Ag 10 wt.%/Al₂O₃, (×) Ag 10 wt.%/Al₂O₃.

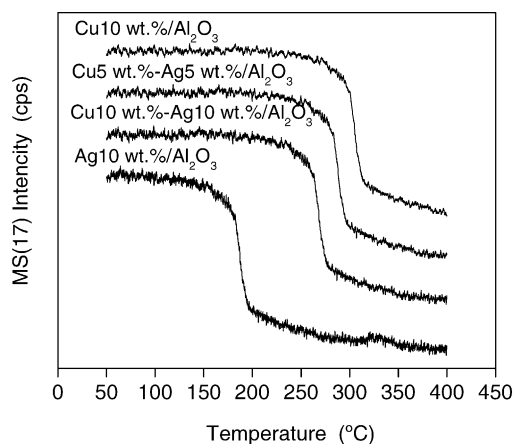


Fig. 3. NH_3 oxidation during NH_3 TPR. Reaction conditions: NH_3 1%; O_2 10%, He 89%; total flow rate, 400N ml/min; catalyst weight, 0.8 g.

with both high activity and selectivity. Increasing Cu and Ag loading (Cu 10 wt.-%-Ag 10 wt.-%/ Al_2O_3) did not lead to the improvement of catalyst oxidation activity. The N_2 selectivity, on the other hand, decreased to a level lower than 80% by increasing Ag loading. Therefore, Cu 5 wt.-%-Ag 5 wt.-%/ Al_2O_3 is the best candidate among the four catalysts in terms of conversion efficiency and selectivity.

3.2. TPR profiles

Figs. 3 and 4 shows NH_3 oxidation and N_2 production profiles measured during the NH_3 TPR experiments over Cu 10 wt.-%/ Al_2O_3 , Cu 5 wt.-%-Ag 5 wt.-%/ Al_2O_3 , Cu 10 wt.-%-Ag 10 wt.-%/ Al_2O_3 , Ag 10 wt.-%/ Al_2O_3 in a flow of NH_3 , O_2 and He. It is clear that the formation of N_2 occurred at the temperature of ammonia decomposition for each catalyst. Ammonia oxidation profiles demonstrated that the Ag-based catalyst (Ag 10 wt.-%/ Al_2O_3) had a much lower conversion starting temperature that of the Cu-based catalyst (Cu 10 wt.-%/ Al_2O_3). The bimetal catalysts, on the other hand, showed a conversion starting temperature be-

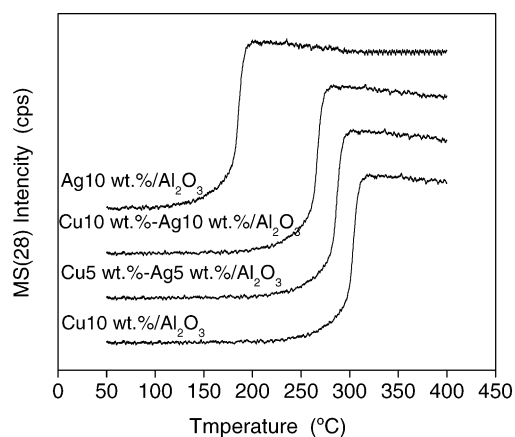


Fig. 4. N_2 production profiles during NH_3 TPR. Reaction conditions: NH_3 1%; O_2 10%; He 89%; total flow rate, 400N ml/min; catalyst weight, 0.8 g.

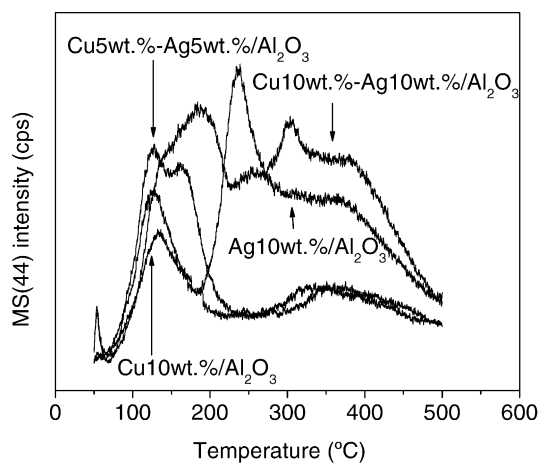


Fig. 5. N_2O production profiles during NH_3 TPR. Reaction conditions: NH_3 1%; O_2 10%; He 89%; total flow rate, 400N ml/min; catalyst weight, 0.8 g.

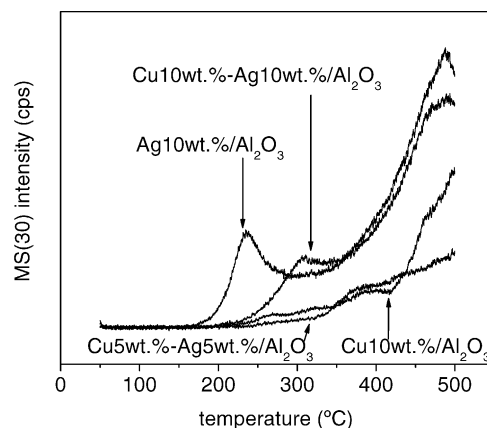


Fig. 6. NO production profiles during NH_3 TPR. Reaction conditions: NH_3 1%; O_2 10%; He 89%; total flow rate, 400N ml/min; catalyst weight, 0.8 g.

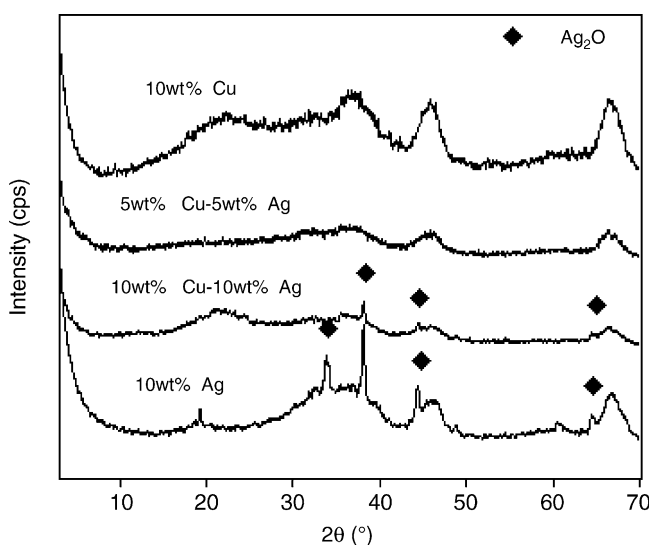


Fig. 7. XRD spectra of the four catalysts.

Table 1
Specific surface area measurement results

Catalysts	Cu 10 wt.%/Al ₂ O ₃	Cu 10 wt.%-Ag 10 wt.%/Al ₂ O ₃	Cu 5 wt.%-Ag 5 wt.%/Al ₂ O ₃	Ag 10 wt.%/Al ₂ O ₃
BET surface area (m ² /g)	224	158	193	188
Pore diameter (Å)	93	123	137	137
Total pore volume (cc/g)	0.52	0.49	0.66	0.64

tween them. Increasing loading of Ag on Cu/Al₂O₃ led to the decrease of conversion starting temperature, further indicating that Ag can be used to decrease the NH₃ conversion temperature of Cu/Al₂O₃.

The production profiles of N₂O and NO, the main side products of selective ammonia oxidation, during NH₃ TPR experiment are shown in Figs. 5 and 6, respectively. N₂O was the main byproduct at temperature lower than 200 °C for all of the four catalysts, and another N₂O peak appeared again at temperature between 240 and 310 °C for Cu 10 wt.%-Ag

10 wt.%/Al₂O₃ and Ag 10 wt.%/Al₂O₃. For Cu 5 wt.%-Ag 5 wt.%/Al₂O₃ and Cu 10 wt.%/Al₂O₃, production of N₂O peak decreased significantly at temperatures higher than 200 °C. Fig. 6 indicates that NO began to be produced with increasing temperature. However, Cu 10 wt.%-Ag 10 wt.%/Al₂O₃ and Ag 10 wt.%/Al₂O₃ produced significantly more NO than Cu 5 wt.%-Ag 5 wt.%/Al₂O₃ and Cu 10 wt.%/Al₂O₃ at their respective complete conversion temperature. Therefore, the low selectivity of Cu 10 wt.%-Ag 10 wt.%/Al₂O₃ and Ag 10 wt.%/Al₂O₃ was due to the pro-

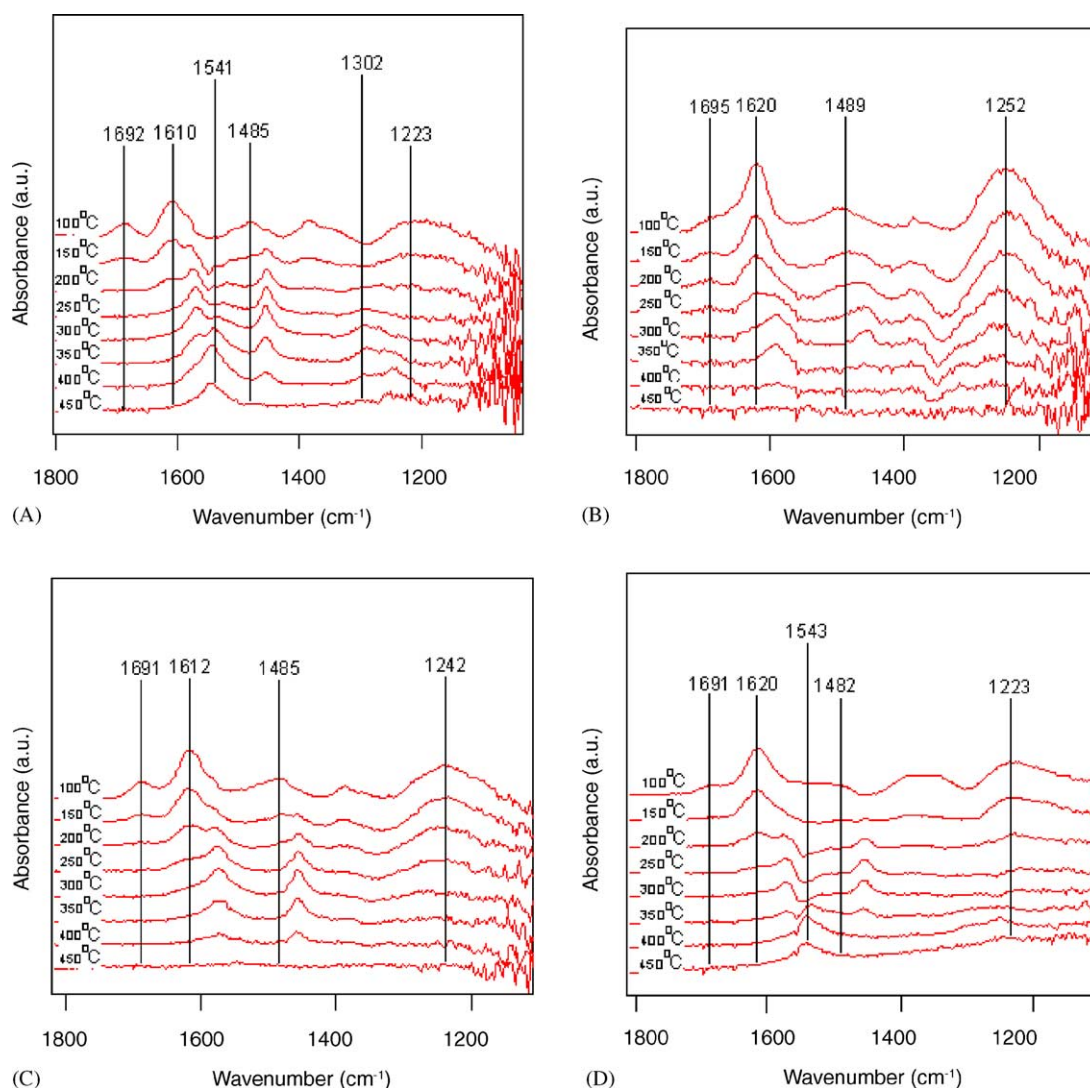


Fig. 8. (A) In situ DRIFT spectra of the surface species on Ag 10 wt.%/Al₂O₃. Total flow = 100N ml/min. (B) In situ DRIFT spectra of the surface species on Cu 10 wt.%/Al₂O₃. Total flow = 100N ml/min. (C) In situ DRIFT spectra of the surface species on Cu 5 wt.%-Ag 5 wt.%/Al₂O₃. Total flow = 100N ml/min. (D) In situ DRIFT spectra of the surface species on Cu 10 wt.%-Ag 10 wt.%/Al₂O₃. Total flow = 100N ml/min.

duction of N_2O and NO during ammonia oxidation. On the other hand, the production of N_2O and NO by Cu 5 wt.-%-Ag 5 wt.-%/ Al_2O_3 and Cu 10 wt.-%/ Al_2O_3 at temperatures higher than 200°C could be neglected, contributing to their high N_2 selectivity.

3.3. XRD results

Fig. 7 shows the XRD spectra of Cu 10 wt.-%/ Al_2O_3 , Cu 5 wt.-%-Ag 5 wt.-%/ Al_2O_3 , Cu 10 wt.-%-Ag 10 wt.-%/ Al_2O_3 , Ag 10 wt.-%/ Al_2O_3 . XRD pattern attributable to crystallized Ag_2O overlapping with $\gamma\text{-Al}_2\text{O}_3$ was observed on the Ag 10 wt.-%/ Al_2O_3 catalyst, which was in accordance with others results [7]. Only $\gamma\text{-Al}_2\text{O}_3$ pattern appears on the Cu 10 wt.-%/ Al_2O_3 and Cu 5 wt.-%-Ag 5 wt.-%/ Al_2O_3 catalysts, whereas weak XRD signals of Ag_2O were observed on the Cu 10 wt.-%-Ag 10 wt.-%/ Al_2O_3 catalyst. It is clear that the Ag_2O crystals could be dispersed when mixed with Cu. It is speculated that the low N_2 selectivity of Ag-based catalyst was possibly related to the formation of Ag_2O phase, considering the results of Fig. 2.

Table 1 shows the specific surface areas (SSA) of the four catalysts. Cu 10 wt.-%/ Al_2O_3 has the largest SSA ($223\text{ m}^2/\text{g}$). The SSA of Cu 5 wt.-%-Ag 5 wt.-%/ Al_2O_3 was $193\text{ m}^2/\text{g}$, significantly lower than that of Cu 10 wt.-%/ Al_2O_3 . Therefore, the increased catalytic activity was not due to the increase of SSA, but to the bimetal composition.

3.4. DRIFT results

Fig. 8A–D shows the in situ DRIFT spectra of Cu 10 wt.-%/ Al_2O_3 , Cu 5 wt.-%-Ag 5 wt.-%/ Al_2O_3 , Cu 10 wt.-%-Ag 10 wt.-%/ Al_2O_3 , Ag 10 wt.-%/ Al_2O_3 in the flow of gas mixture of NH_3 (1%), O_2 (10%) and He (89%) at various temperatures. The bands at $1610\text{--}1620\text{ cm}^{-1}$ and $1200\text{--}1260\text{ cm}^{-1}$ can be assigned to the asymmetric and symmetric deformation modes, respectively, of NH_3 coordinated on Lewis acid sites [5]. The bands at $1687\text{--}1697\text{ cm}^{-1}$ and $1480\text{--}1490\text{ cm}^{-1}$ can be assigned to the asymmetric and symmetric deformation modes, respectively, of NH_3 coordinated on Bronsted acid sites [5]. These bands disappeared with increasing sample temperature. Accompanying with the disappearance of NH_3 bands, new bands at 1541 and 1302 cm^{-1} assigned to nitrate species appeared on Ag 10 wt.-%/ Al_2O_3 and the band at 1541 cm^{-1} on Cu 10 wt.-%-Ag 10 wt.-%/ Al_2O_3 [8,9]. No nitrate bands were observed on Cu 10 wt.-%/ Al_2O_3 and Cu 5 wt.-%-Ag

5 wt.-%/ Al_2O_3 . The above results demonstrated that the formation of NO_x is the main reason of the low selectivity of Ag/ Al_2O_3 and Cu 10 wt.-%-Ag 10 wt.-%/ Al_2O_3 at high temperature.

4. Summary

- Mixing of Ag with Cu improved the NH_3 conversion activity of Cu-based catalyst and the N_2 selectivity of Ag-based catalyst. The Cu 5 wt.-%-Ag 5 wt.-%/ Al_2O_3 displayed a relatively low conversion temperature ($<320^\circ\text{C}$) with a high N_2 selectivity ($>95\%$).
- The Ag 10 wt.-%/ Al_2O_3 showed a strong Ag_2O XRD pattern while the Cu 10 wt.-%/ Al_2O_3 showed no distinct XRD pattern. The low N_2 selectivity of Ag-based catalyst was possibly related to the formation of Ag_2O crystals. Improved N_2 selectivity of Ag-based catalyst was obtained by doping Cu to decrease the crystallized Ag_2O phase.
- On the DRIFT spectra, two nitrate bands appeared on Ag 10 wt.-%/ Al_2O_3 and one nitrate band on Cu 10 wt.-%-Ag 10 wt.-%/ Al_2O_3 at a temperature over 250°C , which were not observed on Cu 10 wt.-%/ Al_2O_3 and Cu 5 wt.-%-Ag 5 wt.-%/ Al_2O_3 . N_2O production profiles during NH_3 TPR demonstrated that significant production of N_2O occurred on Ag 10 wt.-%/ Al_2O_3 and Cu 10 wt.-%-Ag 10 wt.-%/ Al_2O_3 at a temperature between 240 and 310°C . It is speculated that the formation of NO_x and N_2O is the main reason of the low selectivity of Ag/ Al_2O_3 at high temperature.

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