



# The role of silver species on Ag/Al<sub>2</sub>O<sub>3</sub> catalysts for the selective catalytic oxidation of ammonia to nitrogen

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## ABSTRACT

The role of Ag species on Ag/Al<sub>2</sub>O<sub>3</sub> catalyst for the selective catalytic oxidation (SCO) of NH<sub>3</sub> to N<sub>2</sub> was studied using 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared with impregnation, incipient wetness impregnation and sol-gel methods. The catalyst characterization was performed using N<sub>2</sub> adsorption-desorption, UV/Vis, TEM and XRD. O<sub>2</sub>-chemisorption and H<sub>2</sub>-O<sub>2</sub> titration were measured to confirm the metal dispersion on the catalyst. The Ag species state and Ag particle size have significant influence on the Ag/Al<sub>2</sub>O<sub>3</sub> activity and N<sub>2</sub> selectivity of the SCO of NH<sub>3</sub> at low temperature. Ag<sup>0</sup> is proposed to be an active species on the H<sub>2</sub> pretreated catalyst at low temperature (<140 °C). It is evident that well-dispersed and small particle Ag<sup>0</sup> enhances catalytic activity at low temperature, whereas large particle Ag<sup>0</sup> is related to a high N<sub>2</sub> selectivity. In contrast, Ag<sup>+</sup> could also be the active species at temperatures above 140 °C.

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## 1. Introduction

The removal of NH<sub>3</sub> from waste gas streams is becoming increasingly important because of environmental concerns. Selective catalytic oxidation (SCO) of NH<sub>3</sub> to N<sub>2</sub> is an ideal technology for removing NH<sub>3</sub> from waste gases, and it has been of increasing interest in recent years [1–3]. The application areas for the SCO of NH<sub>3</sub> include the treatment of waste gases from various NH<sub>3</sub> emission sources, such as chemical production processes, the selective catalytic reduction (SCR) of NO<sub>x</sub> by urea for diesel powered vehicles, the purification of reformat for fuel-cell systems and the gasification/combustion of biomass for combined heat and power generation.

Previous studies showed that noble metals such as Pt, Ir and Au were active for the reaction of SCO of NH<sub>3</sub> at low temperature, however, the selectivity of N<sub>2</sub> was not satisfied for the reason that the main by-product at low temperature was N<sub>2</sub>O [4–8]. Metal oxide catalysts, namely, MnO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, CuO, CaO, NiO, Bi<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub> [9–17], and many ion-exchanged zeolite catalysts [18–22], have also been investigated for the SCO of NH<sub>3</sub>, but NH<sub>3</sub> conversion levels of these catalysts at low temperature were not high enough to be of practical use.

The Ag-based catalyst used for NH<sub>3</sub> oxidation has been studied by some researchers previously [2,4,5,23,24]. In earlier work, Il'chenko et al. have reported that the specific catalytic activity of metal Ag at 300 °C is lower than that of the precious metals Pt

and Pd [4,5]. Recently, it was reported by Gang et al. that alumina supported Ag (Ag/Al<sub>2</sub>O<sub>3</sub>) catalysts were extremely active for NH<sub>3</sub> oxidation at low temperature, and the performance of the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was even superior to noble metal catalysts [2, 23]. However, the nature of Ag/Al<sub>2</sub>O<sub>3</sub> for the NH<sub>3</sub> oxidation has not been studied in detail, such as the valence state of Ag species and particle size effect on the activity and selectivity of SCO of NH<sub>3</sub>. In addition, the reduced Ag catalysts for NH<sub>3</sub> oxidation are mainly used in oxygenous environment, it is important to investigate the real performance of Ag species under reaction conditions.

In this article, we prepared the Ag/Al<sub>2</sub>O<sub>3</sub> catalysts by different methods and investigated the role of Ag species on the Ag/Al<sub>2</sub>O<sub>3</sub> for its catalytic activity and selectivity of NH<sub>3</sub> oxidation. It has been discovered that the Ag species state and Ag particle size of the Ag/Al<sub>2</sub>O<sub>3</sub> have significant influence on the activity and N<sub>2</sub> selectivity for the SCO of NH<sub>3</sub>. Ag<sup>0</sup> has been proposed as the active species at low temperature, and Ag<sup>+</sup> as the active species at high temperature for the SCO of NH<sub>3</sub>, with the changeover at approximately 140 °C.

## 2. Experimental

### 2.1. Catalyst preparation and H<sub>2</sub> pretreatment

We prepared 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts using three different methods: impregnation, incipient wetness impregnation, and sol-gel methods, denoted IM, IW and SOL, respectively. The catalysts prepared by the IM and IW methods were produced using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder (250 m<sup>2</sup> g<sup>-1</sup>) with an appropriate amount of silver nitrate aqueous solution. The samples were dried at 120 °C overnight and

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then calcined at 600 °C for 3 h in air. The preparation method for the SOL was the same as that in the literature [25] and it was calcined at 600 °C for 6 h in air. The catalysts were sieved into 20–40 mesh powders and pretreated in flowing H<sub>2</sub>/N<sub>2</sub> (20 vol% H<sub>2</sub>, 60 cm<sup>3</sup> min<sup>-1</sup>) at 400 °C for 2 h before testing.

## 2.2. Catalytic tests

### 2.2.1. Catalytic activity test

The SCO activity measurement was carried out in a fixed-bed quartz reactor. In this work, 0.2 g catalyst was used. The reactant gas was obtained by blending different gas flows. The typical reactant gas composition was as follows: 500 ppm NH<sub>3</sub>, 10 vol% O<sub>2</sub>, and balance N<sub>2</sub>. The total flow rate was 200 cm<sup>3</sup> min<sup>-1</sup> ( $W/F = 0.06 \text{ g s cm}^{-3}$ ). NH<sub>3</sub>, O<sub>2</sub>, and N<sub>2</sub> flow rates were controlled by mass flow controllers. The inlet and outlet gas compositions were analyzed by an on-line NEXUS 670-FTIR spectrophotometer fitted with a gas cell of volume 200 cm<sup>3</sup>. These conditions are defined as standard conditions.

In order to investigate the pre-treatment effects, we tested the activity of the fresh Ag/Al<sub>2</sub>O<sub>3</sub> (IM) under the standard conditions and compared it with the activity of the H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> (IM).

### 2.2.2. Evolution with time-on-stream at 160 °C

The H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> (IM) catalyst was fed with the reactant mixture (standard conditions) at 160 °C, and the evolution of the NH<sub>3</sub> conversion and N<sub>2</sub> selectivity were recorded for the next 48 h at 160 °C.

### 2.2.3. Temperature cycle

The H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> (IM) catalyst was heated from room temperature to 220 °C and cooled to room temperature under the standard conditions for 5 times.

## 2.3. Characterization of catalysts

The N<sub>2</sub> adsorption-desorption isotherms were obtained at -196 °C over the whole range of relative pressures, using a Quantasorb-18 automatic instrument (Quanta Chrome Instrument Co.). Specific areas were computed from these isotherms by applying the Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated by the BJH method. Before measurement, the samples were treated by degassing at 300 °C for 4 h.

Powder X-ray diffraction (XRD) measurements of the catalysts were carried out on a Rigaku D/max-RB X-Ray Diffractometer (Japan) using CuK $\alpha$  radiation and operating at 40 kV and 40 mA. The patterns were taken over the  $2\theta$  range from 20 to 70° at a scan speed of 6° min<sup>-1</sup>.

Diffuse-reflectance UV/Vis spectra (UV/Vis) were recorded under ambient conditions on a U-3010 (Hitachi) spectrometer with a standard diffuse reflectance unit. The range was 190–850 nm and the scan rate was 300 nm min<sup>-1</sup>. The measured spectra were converted into Kubelka-Munk functions and deconvoluted into Gaussian subbands that could be quantitatively assigned to the different Ag species [26–33].

Transmission electron microscopy (TEM) characterizations were carried out using an H-7500 (Hitachi) instrument. The accelerating voltage for the microscope was 80 kV and the point resolution was 0.36 nm. 200–300 particles were counted to evaluate the particle size (diameter) distribution.

The global dispersion (%) of Ag and the mean particle size (MPS) (nm) in the prepared catalysts were determined by O<sub>2</sub>-chemisorption at 170 °C using a Quantasorb-18 (Quanta Chrome Instrument Co.) at a pressure range of 40 to 200 Torr of O<sub>2</sub>, according to Ref. [34]. Before the O<sub>2</sub>-chemisorption experiments, the

samples were reduced in a 5 vol% H<sub>2</sub>/Ar stream (40 cm<sup>3</sup> min<sup>-1</sup>) by heating from room temperature to 400 °C with a heating rate of 10 °C min<sup>-1</sup>, and then holding at this temperature for 2 h. Metal dispersion and MPS were calculated by the Langmuir method according to a method adapted from the literature [35]. For dispersion measurements, we relied on the total adsorption isotherms and stoichiometries of Ag/O<sub>2</sub> = 2 [34,35].

H<sub>2</sub>-O<sub>2</sub> titration has also been a common method for the detection of Ag dispersion. We therefore measured the Ag dispersion using a H<sub>2</sub>-O<sub>2</sub> titration pulse method in a homemade pulse flow system equipped with a computer-interfaced quadrupole mass spectrometer (Hiden HPR 20). Prior to the H<sub>2</sub>-O<sub>2</sub> titration, 100 mg of sample was reduced in 5 vol% H<sub>2</sub>/Ar (40 cm<sup>3</sup> min<sup>-1</sup>, 10 °C min<sup>-1</sup>) at 400 °C for 2 h. Then He gas (40 cm<sup>3</sup> min<sup>-1</sup>) was passed over the sample for 1 h. After cooling to 170 °C in He, the O<sub>2</sub> adsorption experiment was performed, followed by flushing with He (40 cm<sup>3</sup> min<sup>-1</sup>), then the introduction of H<sub>2</sub> pulses (1 cm<sup>3</sup> of 5 vol% H<sub>2</sub>/Ar). The stoichiometries of Ag/O<sub>2</sub> = 2, Ag/H<sub>2</sub> = 1 were assumed [34]. On the basis of these dispersion (*D*) data, the crystallite size could be estimated from the expression  $d \text{ (nm)} = 1.34/D$ , assuming spherical Ag crystallites [36]. We note that there have been a number of studies of O<sub>2</sub>-chemisorption and H<sub>2</sub>-O<sub>2</sub> titration on Ag. We selected the reduction temperature 400 °C (10 °C min<sup>-1</sup>) to ensure that the degree of reduction in these conditions was approximately 100%, the same condition as before the activity test.

## 3. Results

### 3.1. NH<sub>3</sub> oxidation over 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts

To elucidate the effects of the preparation methods, 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared using three different methods were tested for the SCO of NH<sub>3</sub> at various temperatures. As can be seen in Fig. 1, IW and IM behaved similarly and they had higher NH<sub>3</sub> conversions at low temperature, quite different from SOL. However, the SOL showed better selectivity to N<sub>2</sub> than the other two catalysts. It is noteworthy that N<sub>2</sub>O was the main by-product produced over the catalysts IM and IW at lower temperatures.

As shown in Fig. 2, H<sub>2</sub> pretreatment significantly improved the low temperature activity of the Ag/Al<sub>2</sub>O<sub>3</sub> (IM), showing over 95% conversion of NH<sub>3</sub> at 140 °C and reaching 100% at 160 °C. However, no NH<sub>3</sub> conversion was obtained over fresh Ag/Al<sub>2</sub>O<sub>3</sub> (IM) at 140 °C, but complete conversion at 220 °C.

Since the NH<sub>3</sub> conversion reached 100% at 160 °C over the H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> (IM) catalyst, we kept the temperature at 160 °C for more than 48 h to continuously test the activity of the reduced Ag/Al<sub>2</sub>O<sub>3</sub> catalyst (shown in Fig. 3). It was discovered that high NH<sub>3</sub> conversion over the H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> at 160 °C was retained for at least 48 h, while the selectivity of N<sub>2</sub> increased slightly (from 46% to 50%).

As shown in Fig. 2, the NH<sub>3</sub> conversion over the fresh and H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> catalysts increased with the temperature; complete conversions of NH<sub>3</sub> were obtained at 220 and 160 °C. Temperature cycle test was performed on the H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> from room temperature to 220 °C for 5 times under the standard conditions. The SCO of NH<sub>3</sub> over the catalyst was tested at various temperatures. The result is shown in Fig. 4. It is significant that the NH<sub>3</sub> conversion at low temperature decreased gradually over the 5 reaction cycles, but the selectivity for N<sub>2</sub> formation showed the opposite behavior. In all the 5 cycles, the NH<sub>3</sub> conversion reached 100% at 220 °C.

We compared the performance of our Ag/Al<sub>2</sub>O<sub>3</sub> catalysts with the results of the reported highly active noble metal catalysts [3, 8,15] in Table 1. Since the reaction conditions of NH<sub>3</sub> oxidation used in these literatures were different with this work, we also

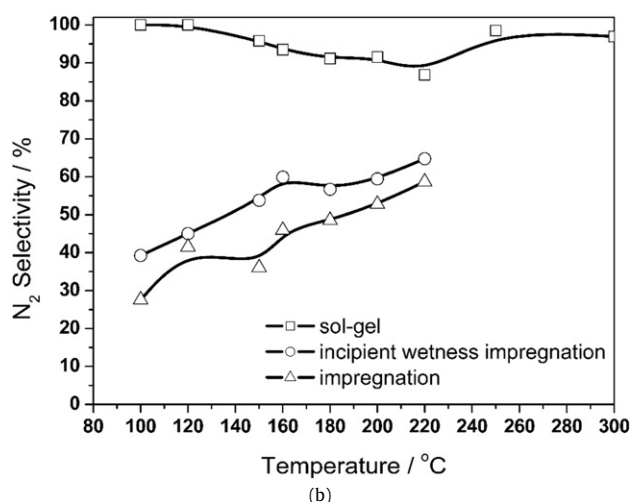
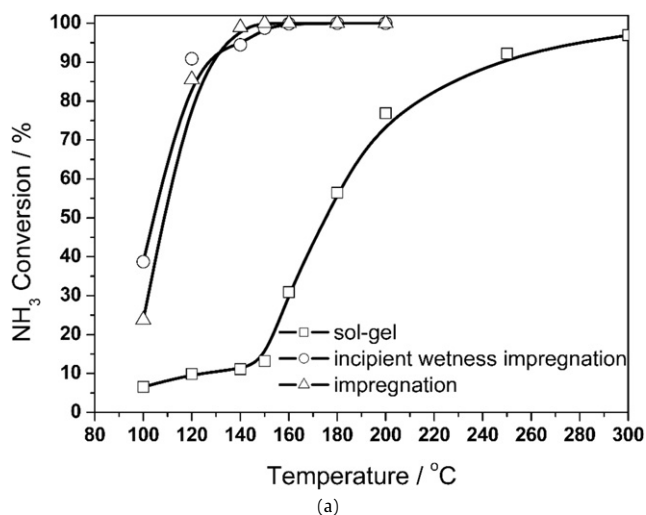


Fig. 1. NH<sub>3</sub> conversion (a) and N<sub>2</sub> selectivity (b) at different temperatures over the three H<sub>2</sub> pretreated 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by: sol-gel (SOL), incipient wetness impregnation (IW) and impregnation (IM) methods.

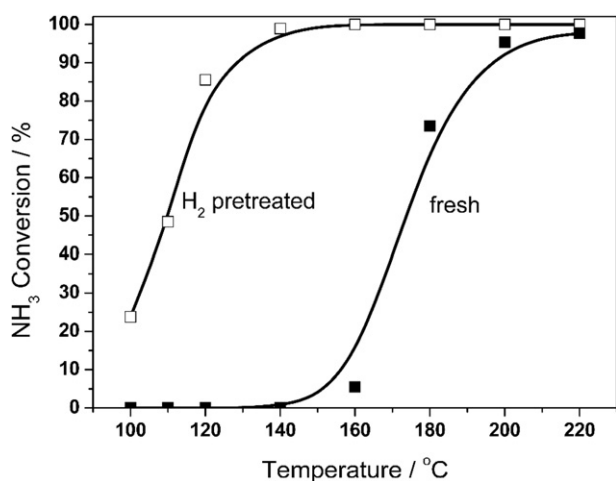


Fig. 2. NH<sub>3</sub> conversion over the fresh (■) and H<sub>2</sub> pretreated (□) 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by impregnation method.

tested the activity of two noble metal catalysts prepared by impregnation method under the same conditions of this work in our laboratory. Table 1 shows the performance of the Ag/Al<sub>2</sub>O<sub>3</sub> catalysts compared with the noble metal catalysts. It can be seen that the performance of Ag/Al<sub>2</sub>O<sub>3</sub> catalysts (IM and IW) are superior to

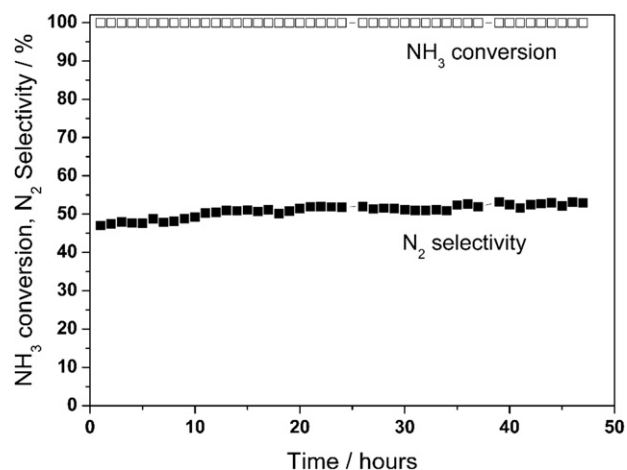


Fig. 3. NH<sub>3</sub> conversion (□) and N<sub>2</sub> selectivity (■) over the H<sub>2</sub> pretreated 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by impregnation method (IM) at 160 °C for 48 h under the standard conditions.

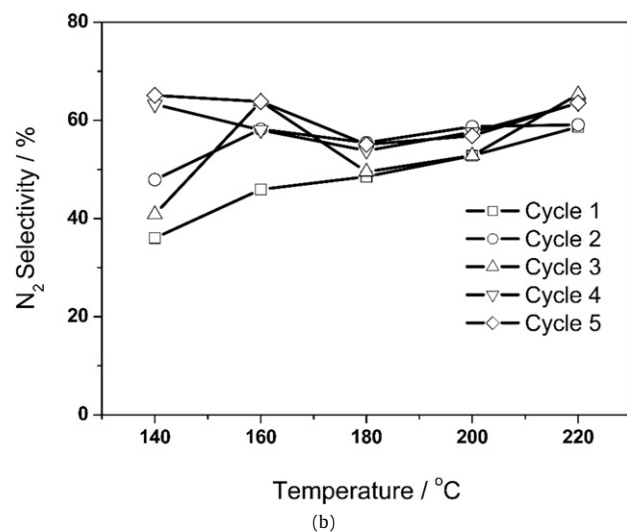
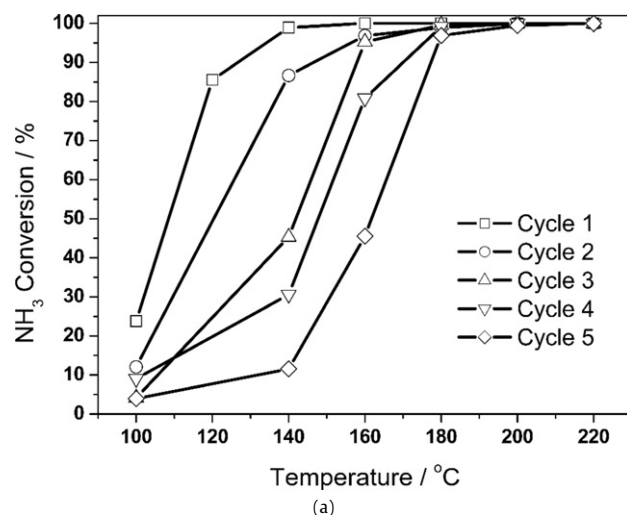


Fig. 4. NH<sub>3</sub> conversion (a) and N<sub>2</sub> selectivity (b) over the H<sub>2</sub> pretreated 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by impregnation method (IM) over 5 cycles under the standard conditions.

that of noble metal catalysts in low temperature activity as well as the Ag/Al<sub>2</sub>O<sub>3</sub> (SOL) in N<sub>2</sub> selectivity. With further improvement, this catalyst is promising to be used instead of noble metal catalysts at low temperature (<200 °C).

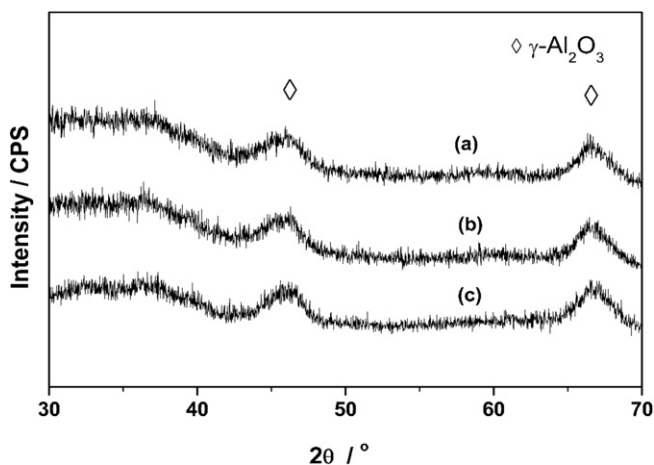
**Table 1**  
The activity and N<sub>2</sub> selectivity of various catalysts for NH<sub>3</sub> oxidation.

Catalysts	Temperature (°C)	NH <sub>3</sub> conversion (%)	N <sub>2</sub> selectivity (%)	References
10 wt% Ag/Al <sub>2</sub> O <sub>3</sub> (IM)	110	48	45	This study <sup>a</sup>
(H <sub>2</sub> pretreated)	140	96	41	
10 wt% Ag/Al <sub>2</sub> O <sub>3</sub> (IW)	110	52	41	This study <sup>a</sup>
(H <sub>2</sub> pretreated)	140	94	54	
10 wt% Ag/Al <sub>2</sub> O <sub>3</sub> (SOL)	180	56	91	This study <sup>a</sup>
(H <sub>2</sub> pretreated)	240	90	95	
1 wt% Pd/Al <sub>2</sub> O <sub>3</sub>	140	34	48	This study <sup>a</sup>
(H <sub>2</sub> pretreated) <sup>b</sup>	160	86	75	
1 wt% Pt/Al <sub>2</sub> O <sub>3</sub>	220	40	76	This study <sup>a</sup>
(H <sub>2</sub> pretreated) <sup>c</sup>	240	83	70	
0.6 wt%	200	45	99	[3]
Pt-Fe-ZSM-5	250	99	92	
Au/CuO/Al <sub>2</sub> O <sub>3</sub> (Cu:Al = 1:10)	211	50	94	[8]
1.2 wt% Ir/Al <sub>2</sub> O <sub>3</sub>	180	52	88	[15]
(H <sub>2</sub> pretreated)	200	100	84	

<sup>a</sup> Reaction conditions: NH<sub>3</sub>, 500 ppm; O<sub>2</sub>, 10 vol%; N<sub>2</sub> as balance; flow rate, 200 cm<sup>3</sup> min<sup>-1</sup>; catalyst weight, 0.2 g (*W/F* = 0.06 g s cm<sup>-3</sup>).

<sup>b</sup> 1 wt% Pd/Al<sub>2</sub>O<sub>3</sub> prepared by impregnation method.

<sup>c</sup> 1 wt% Pt/Al<sub>2</sub>O<sub>3</sub> prepared by impregnation method.



**Fig. 5.** XRD profiles of the fresh 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by impregnation (IM) (a), incipient wetness impregnation (IW) (b) and sol-gel (SOL) (c) methods.

**Table 2**

BET surface area, pore size and mean particle size of the fresh 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by impregnation (IM), incipient wetness impregnation (IW) and sol-gel (SOL) methods.

Catalysts	BET (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	Pore volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>a</sup>	Average pore diameter (Å) <sup>a</sup>	Mean particle size (nm) <sup>b</sup>
IM	249	0.822	129	14
IW	248	0.709	111	14
SOL	174	0.201	42.8	21

<sup>a</sup> Determined by BET.

<sup>b</sup> Determined by TEM.

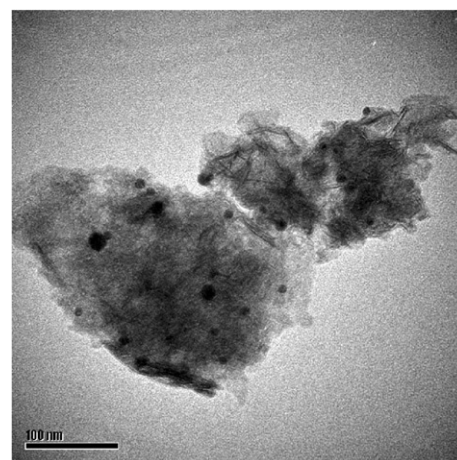
## 3.2. Characterization

### 3.2.1. X-ray diffraction

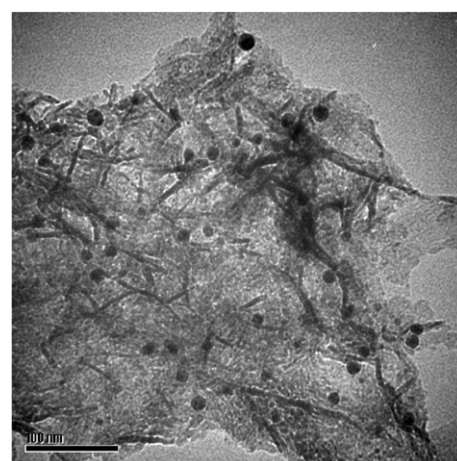
Fig. 5 shows the XRD patterns of the fresh 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by the three methods. Only the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystallites were evident and no Ag<sub>2</sub>O or metallic Ag<sup>0</sup> crystallites appeared.

### 3.2.2. Transmission electron microscopy

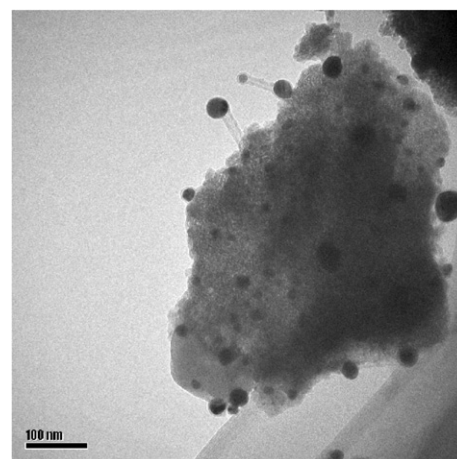
Fig. 6 shows the TEM images of the 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by the three different methods to demonstrate the distribution of Ag particles. It can be seen that small Ag particles formed on the IM and IW catalysts (Fig. 6a and b), whereas large Ag par-



(a)



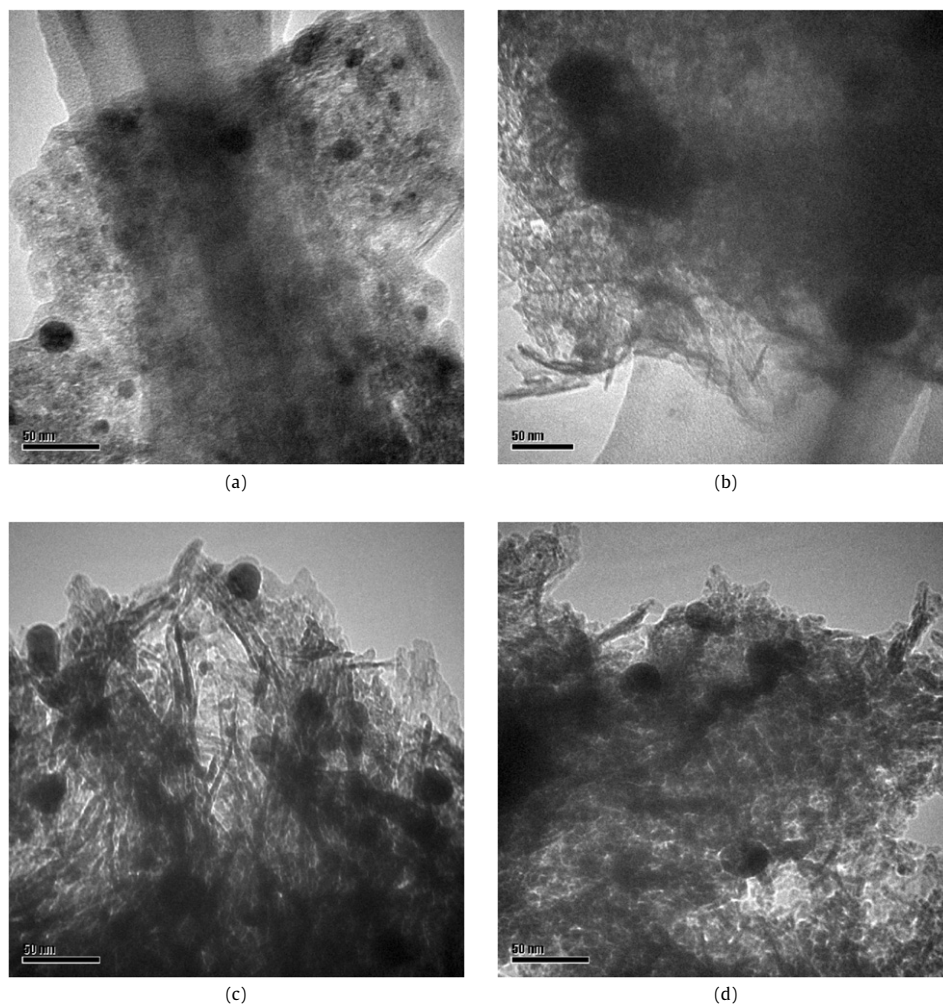
(b)



(c)

**Fig. 6.** TEM images of the fresh 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by impregnation (IM) (a), incipient wetness impregnation (IW) (b) and sol-gel (SOL) (c) methods.

ticles tended to form on the SOL catalyst (Fig. 6c). The distribution of the Ag particles on the IM and IW catalysts were similar, ranging from 3.5 to 25 nm in diameter (Fig. 6a and b), whereas there was a broad distribution on the SOL catalyst, from 12 to 50 nm in diameter (Fig. 6c). Statistical calculations on the particles measured in the TEM images were used to determine the MPS of the Ag particles on the three fresh 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts (Table 2). The diameters of the particles in nanometer were calculated assuming spherical particle form. Particles under 2 nm were not detectable



**Fig. 7.** TEM images of 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by impregnation method (IM): H<sub>2</sub> pretreated (a); after testing at 160 °C for 48 h (b); after 1 test cycle (c); after 5 test cycles (d).

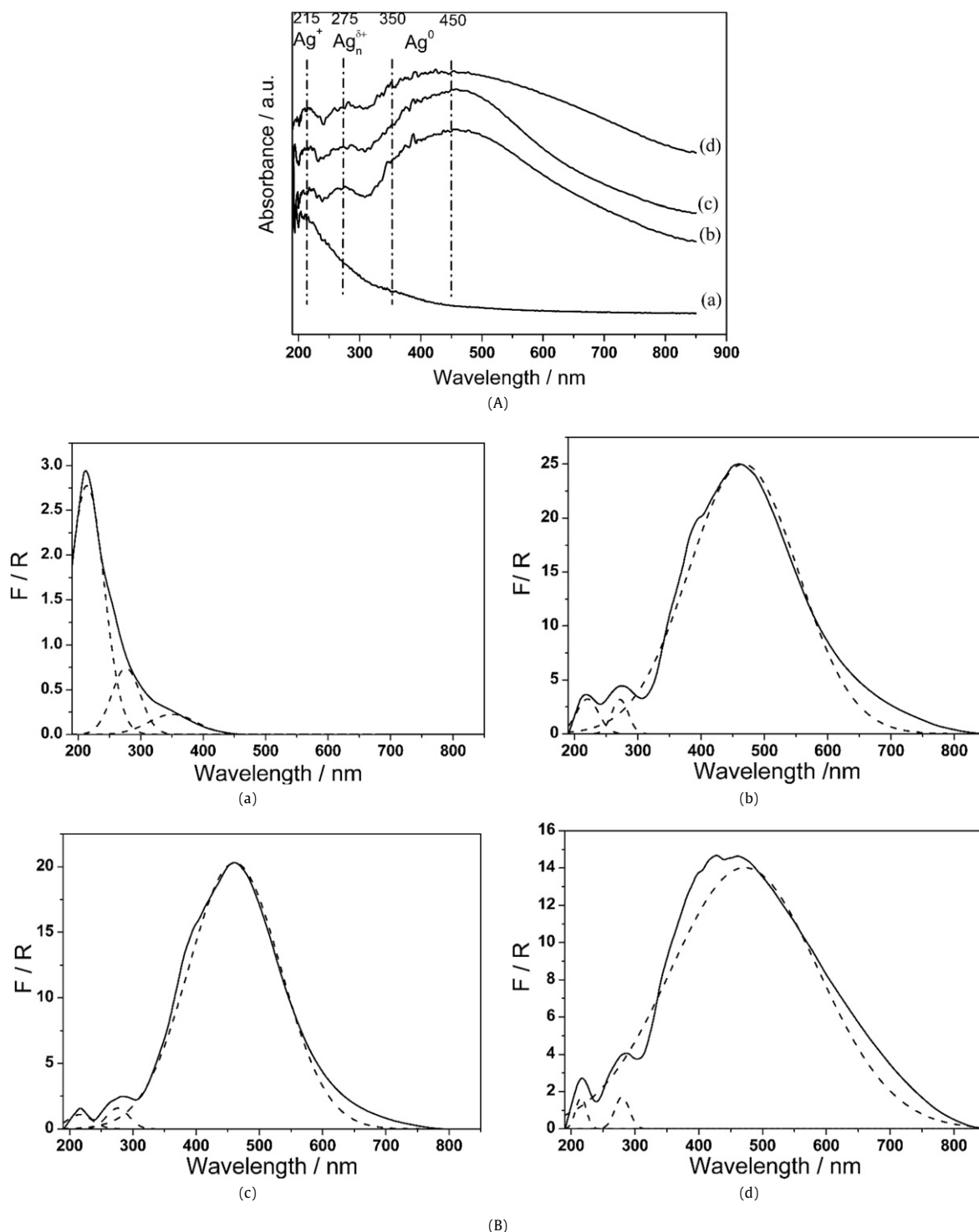
in this TEM experiment, so they have not been counted in the MPS. As shown in Table 2, the catalyst (SOL) with the lower BET surface area had a larger MPS than the other two catalysts; catalysts IM and IW with the larger surface areas had smaller MPS similarly. This demonstrates that the high surface areas of catalysts IM and IW favor the high dispersion of Ag species, thus small Ag particles are formed on the support. It also indicates that the preparation method has a significant influence on the BET surface area, pore size and Ag particle size distribution of the Ag/Al<sub>2</sub>O<sub>3</sub> catalysts. Combining with our XRD spectra (Fig. 5), it clearly shows that the Ag species is well dispersed on the Ag/Al<sub>2</sub>O<sub>3</sub> catalysts (IM and IW), but is not well dispersed on the SOL. However, our XRD pattern of the Ag/Al<sub>2</sub>O<sub>3</sub> (SOL) (Fig. 5) shows no Ag<sub>2</sub>O or metallic Ag<sup>0</sup> crystallites appeared, although the Ag particles on the SOL are quite large (12–50 nm) (Fig. 6c). This might be because that Ag species on the Ag/Al<sub>2</sub>O<sub>3</sub> (SOL) was amorphous phase, thus the XRD spectra could not detect it.

Fig. 7 compares the TEM images of the H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> (IM) catalyst, a catalyst (IM) after the stability test (held at 160 °C for 48 h under standard conditions) and two cycled catalysts (IM) (tested for 1 and 5 cycles to 220 °C under standard conditions). As can be seen, some small Ag particles aggregated into larger ones after the stability test (Fig. 7b); the largest particle was about 50 nm in diameter. As shown in Fig. 7c, some Ag particles also aggregated into larger ones after 1 test cycle; the largest particle was nearly 40 nm in diameter. Aggregation of Ag particles was more evident after 5 test cycles (Fig. 7d).

The low temperature activities ( $\leq 160$  °C) of Ag/Al<sub>2</sub>O<sub>3</sub> decreased gradually over the test cycles (Fig. 4), which is coinciding with the aggregation of the Ag particles (Fig. 7c and d). It seemed that this particle size effect had an influence upon the low temperature activity. The result of the stability test showed that the 100% NH<sub>3</sub> conversion did not decrease after retention at 160 °C for about 50 h (Fig. 3). The TEM result (Fig. 7b) showed that some Ag particles clumped together but this did not influence the high NH<sub>3</sub> conversion of the Ag/Al<sub>2</sub>O<sub>3</sub> at 160 °C (Fig. 3), this will be discussed in the following section. We also discovered that the Ag particle size of H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> (IM) (Fig. 7a) was smaller than that of the fresh Ag/Al<sub>2</sub>O<sub>3</sub> (IM) (Fig. 6a).

### 3.2.3. Diffuse-reflectance UV/Vis spectra

UV/Vis was taken to discover the details of the state of the supported Ag. Fig. 8 shows the spectra of the fresh Ag/Al<sub>2</sub>O<sub>3</sub> (IM) and the three H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> catalysts. UV/Vis analysis demonstrates the existence of different states of the Ag species, after subtraction of the Al<sub>2</sub>O<sub>3</sub> spectrum. As shown in Fig. 8A, the fresh Ag/Al<sub>2</sub>O<sub>3</sub> (IM) showed broad absorption bands at around 215, 275 and 350 nm, while the three H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> catalysts gave an additional broad band at around 450 nm. The band at 215 nm is attributed to the 4d<sup>10</sup> to 4d<sup>9</sup>5s<sup>1</sup> transition of highly dispersed Ag<sup>+</sup> ions [28,29], 275 nm is assigned to small Ag<sub>n</sub><sup>δ+</sup> clusters [30–32] and the bands at 350 and 450 nm are attributed to metallic silver (Ag<sup>0</sup>) particles [28–32]. Sato et al. confirmed an absorption band of metallic Ag<sub>n</sub> clusters at 352 nm for 4% Ag/Al<sub>2</sub>O<sub>3</sub> [30]. Bog-



**Fig. 8.** Diffuse reflectance UV/Vis spectra (A) and deconvoluted subbands (B) of the fresh 10 wt%  $\text{Ag}/\text{Al}_2\text{O}_3$  prepared by impregnation method (IM) (a) and three  $\text{H}_2$  pretreated catalysts prepared by IM (b), incipient wetness impregnation (IW) (c) and sol-gel (SOL) (d) methods.

danchikova et al. also reported an absorption band of  $\text{Ag}^0$  at a wavelength  $>390$  nm for reduced  $\text{Ag}/\text{Al}_2\text{O}_3$  [29]. Accordingly, we can estimate that the bands at 350 and 450 nm are due to metallic  $\text{Ag}^0$  particles.

As shown in Fig. 8B, the measured spectra of the  $\text{Ag}/\text{Al}_2\text{O}_3$  catalysts were converted into Kubelka–Munk functions and deconvoluted into Gaussian subbands that could be assigned to different Ag species [26–33]. The deconvolution was carried out based on the above assignments and the relative intensities of these subbands are listed in Table 3, including the corresponding percentage

of the different Ag species. We estimated the amount of the different Ag species by multiplying the relative subband intensities by the total Ag content (10 wt%) in the  $\text{Al}_2\text{O}_3$ . The quantification of the different Ag species is shown in Table 3 as follows:  $I_1$  for  $\text{Ag}^+$  ( $\lambda < 238$  nm),  $I_2$  for  $\text{Ag}_n^+$  ( $238 < \lambda < 320$  nm), and  $I_3$  for  $\text{Ag}^0$  ( $\lambda > 320$  nm). However, these subbands should be understood as a description of a semi-quantitative distribution of different Ag species. Despite the uncertainty of the deconvolution procedure, the quantification in Table 3 provides a valuable indication of the relative amount of various Ag species among the catalysts investigated.

**Table 3**

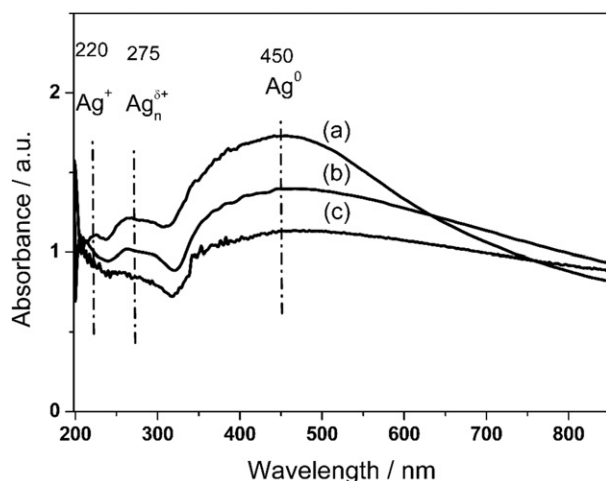
The percentage of integrated area of the bands derived from deconvolution of the UV/Vis spectra in Fig. 8 and the corresponding Ag species dispersion on fresh and H<sub>2</sub> pretreated 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> samples prepared by impregnation (IM), incipient wetness impregnation (IW) and sol-gel (SOL) methods.

Catalysts	Ag <sup>+</sup>		Ag <sub>n</sub> <sup>δ+</sup>		Ag <sup>0</sup>	
	I <sub>1</sub> <sup>a</sup> (%)	wt%	I <sub>2</sub> <sup>b</sup> (%)	wt%	I <sub>3</sub> <sup>c</sup> (%)	wt%
Fresh Ag/Al <sub>2</sub> O <sub>3</sub> (IM)	71.5	7.15	19.6	1.96	8.9	0.89
H <sub>2</sub> pretreated (IM)	2.4	0.24	1.8	0.18	95.9	9.59
H <sub>2</sub> pretreated (IW)	1.3	0.13	1.8	0.18	96.9	9.69
H <sub>2</sub> pretreated (SOL)	0.9	0.09	1.2	0.12	98.0	9.80

<sup>a</sup> I<sub>1</sub> for Ag<sup>+</sup> (band at λ < 238 nm).

<sup>b</sup> I<sub>2</sub> for Ag<sub>n</sub><sup>δ+</sup> (band at 238 < λ < 320 nm).

<sup>c</sup> I<sub>3</sub> for Ag<sup>0</sup> (band at λ > 320 nm).



**Fig. 9.** Diffuse reflectance UV/Vis spectra of 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by impregnation method (IM): after the stability test (held at 160 °C for 48 h) (a); after 1 test cycle (b) and after 5 test cycles (c).

For fresh Ag/Al<sub>2</sub>O<sub>3</sub> (IM), Ag<sup>+</sup> is the major Ag species on the Al<sub>2</sub>O<sub>3</sub>. For the three H<sub>2</sub> pretreated catalysts, Ag<sup>0</sup> is the main Ag species on the support (Table 3). This proves that most of the Ag<sub>x</sub>O on the Al<sub>2</sub>O<sub>3</sub> can be reduced to Ag<sup>0</sup> by H<sub>2</sub> pretreatment. Combining with our activity test result (Fig. 2), the appearance of Ag<sup>0</sup> should be the reason for the improvement of NH<sub>3</sub> conversion at low temperature. Although Ag<sup>0</sup> is the main Ag species on the three H<sub>2</sub> pretreated catalysts, one can still see that the three catalysts showed different behavior for the SCO of NH<sub>3</sub> (Fig. 1), and this will be discussed in the following section.

Fig. 9 shows the UV/Vis result of the Ag species in the Ag/Al<sub>2</sub>O<sub>3</sub> catalysts (IM) after the cyclic (room temperature –220 °C) and stability tests (160 °C). Table 4 compares the relative percentage of the Ag species of the three Ag/Al<sub>2</sub>O<sub>3</sub> catalysts. It is evident that some Ag<sup>0</sup> species were oxidized to Ag<sup>+</sup> after 1 test cycle, and this is more evident after 5 cycles. Combining the cyclic test (Fig. 4) and TEM (Figs. 7c and 7d) results, we discovered that besides the Ag particle size effect, Ag<sup>0</sup> oxidation was another important reason for the variation of NH<sub>3</sub> conversion and N<sub>2</sub> selectivity at low temperature. However, Ag<sup>0</sup> was hardly oxidized after testing at 160 °C for about 50 h (Table 4). According to our stability test result (Fig. 3), the NH<sub>3</sub> conversion at this condition did not decrease either. These results also indicate that Ag<sup>0</sup> is the main active species on the H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> (IM) at this temperature, and that the metallic Ag<sup>0</sup> was retained at this condition. The TEM (Fig. 7b) result showed that some Ag<sup>0</sup> particles aggregated together, while the high NH<sub>3</sub> conversion could be retained at 160 °C. This reason may be that the Ag active sites are still enough for the high NH<sub>3</sub> conversion in spite of the aggregation of some Ag<sup>0</sup> particles. In fact, we observed

**Table 4**

The percentage of integrated area of the bands derived from deconvolution of the UV/Vis spectra in Fig. 9 and the corresponding Ag species dispersion on H<sub>2</sub> pretreated 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> samples (prepared by impregnation method) after cyclic and stability tests.

Catalysts	Ag <sup>+</sup>		Ag <sub>n</sub> <sup>δ+</sup>		Ag <sup>0</sup>	
	I <sub>1</sub> <sup>a</sup> (%)	wt%	I <sub>2</sub> <sup>b</sup> (%)	wt%	I <sub>3</sub> <sup>c</sup> (%)	wt%
Tested 1 cycle	15.0	1.50	8.0	0.80	77.0	7.70
Tested 5 cycles	19.3	1.93	14.4	1.44	66.3	6.63
After stability test	4.8	0.48	4.0	0.40	91.2	9.12

<sup>a</sup> I<sub>1</sub> for Ag<sup>+</sup> (band at λ < 238 nm).

<sup>b</sup> I<sub>2</sub> for Ag<sub>n</sub><sup>δ+</sup> (band at 238 < λ < 320 nm).

<sup>c</sup> I<sub>3</sub> for Ag<sup>0</sup> (band at λ > 320 nm).

the decreases of NH<sub>3</sub> conversion with aggregation of Ag<sup>0</sup> particles in higher gas hourly space velocity (GHSV) experiments.

### 3.2.4. O<sub>2</sub>-chemisorption and H<sub>2</sub>-O<sub>2</sub> titration

The Ag dispersion on Al<sub>2</sub>O<sub>3</sub> and the MPS of the three H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> catalysts shown in Table 5 were determined by O<sub>2</sub> adsorption and H<sub>2</sub>-O<sub>2</sub> titration pulse methods, which were performed at 170 °C as suggested in the literature [34,36]. The Ag dispersions of the three catalysts, as determined by the two methods, were similar. It can be seen that the MPS of catalysts IM and IW determined from O<sub>2</sub> adsorption and H<sub>2</sub>-O<sub>2</sub> titration was consistently smaller than that of the SOL. According to our acquired turn over frequency (TOF) for NH<sub>3</sub> at 110 °C (Table 5), catalysts IM and IW, with similar small MPS, displayed almost the same behavior toward NH<sub>3</sub> oxidation. However, catalyst SOL, with larger MPS, had a much lower activity than the others. We conclude that highly dispersed Ag<sup>0</sup> particles favor higher activity at low temperature.

The MPS of the H<sub>2</sub> pretreated catalyst determined by the O<sub>2</sub> adsorption and H<sub>2</sub>-O<sub>2</sub> titration pulse methods (Table 5) was less than that of the fresh Ag/Al<sub>2</sub>O<sub>3</sub> (Table 2), which was consistent with the TEM results (Figs. 6a and 7a). UV/Vis results indicate that Ag<sub>x</sub>O on the Al<sub>2</sub>O<sub>3</sub> could be reduced to Ag<sup>0</sup> after H<sub>2</sub> reduction, so some small Ag<sup>0</sup> particles appeared on the support. These new Ag<sup>0</sup> particles must be the reason for the MPS variation for the H<sub>2</sub> pretreated catalyst.

## 4. Discussion

H<sub>2</sub> pretreatment significantly improved the low temperature activity of Ag/Al<sub>2</sub>O<sub>3</sub> (IM) for the SCO of NH<sub>3</sub> (Fig. 2). The NH<sub>3</sub> conversion over H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> (IM) reached over 95% at 140 °C, while no NH<sub>3</sub> conversion was obtained over fresh Ag/Al<sub>2</sub>O<sub>3</sub> (IM) at this temperature. Ag<sup>0</sup> was the major Ag species on the H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> (Fig. 8) while Ag<sup>+</sup> was the main Ag species on the fresh catalyst (IM) (Table 3). We infer that Ag<sup>0</sup> is the active species of Ag/Al<sub>2</sub>O<sub>3</sub> at low temperature (<140 °C). However, the fresh Ag/Al<sub>2</sub>O<sub>3</sub> was also active at temperatures above 140 °C, therefore Ag<sup>+</sup> could also be the active species at these higher temperatures. This proves that the active species of Ag/Al<sub>2</sub>O<sub>3</sub> might be different in different temperature ranges.

Catalysts prepared by three different methods behaved differently. Ag/Al<sub>2</sub>O<sub>3</sub> (SOL) had the lowest activity but the best N<sub>2</sub> selectivity at low temperature. Catalysts IM and IW behaved similarly and had better activities at low temperature whereas their N<sub>2</sub> selectivity was not good. According to N<sub>2</sub> adsorption-desorption, TEM, O<sub>2</sub>-chemisorption and H<sub>2</sub>-O<sub>2</sub> titration results, catalyst (SOL) with a lower BET surface area and larger Ag<sup>0</sup> particles did not show good activity at low temperature. Catalysts IM and IW, with highly dispersed Ag<sup>0</sup> particles, had higher activity for the SCO of NH<sub>3</sub> at low temperature. Combining these results with the UV/Vis characterization (Fig. 8) of the three H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> catalysts, we conclude that Ag<sup>0</sup> was the main Ag species on the

**Table 5**  
Ag dispersion, mean particle size and turn over frequency (TOF)<sup>a</sup> of three H<sub>2</sub> pretreated 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by impregnation (IM), incipient wetness impregnation (IW) and sol-gel (SOL) methods.

Catalysts	Dispersion (%) <sup>b</sup>	Mean particle size (nm) <sup>b</sup>	TOF 10 <sup>-3</sup> (s <sup>-1</sup> ) <sup>d</sup>	Dispersion (%) <sup>c</sup>	Mean particle size (nm) <sup>c</sup>	TOF 10 <sup>-3</sup> (s <sup>-1</sup> ) <sup>d</sup>
IM	30.3	3.9	0.64	34.2	3.9	0.57
IW	39.7	3.0	0.53	39.2	3.4	0.53
SOL	17.3	6.8	0.19	16.6	8.1	0.20

<sup>a</sup> Reaction conditions: catalyst 0.2 g; NH<sub>3</sub> 500 ppm; O<sub>2</sub> 10%; total flow rates 200 cm<sup>3</sup> min<sup>-1</sup>; temperature 110 °C.

<sup>b</sup> Determined by O<sub>2</sub>-chemisorption.

<sup>c</sup> Determined by H<sub>2</sub>-O<sub>2</sub>-titration.

<sup>d</sup> The TOF here was calculated by the moles of NH<sub>3</sub> converted per mole of Ag in the whole catalyst per second.

three catalysts. However, their activity and N<sub>2</sub> selectivity for the SCO of NH<sub>3</sub> were still different, the main differences being their Ag dispersion and Ag<sup>0</sup> particle size (Table 5). Highly dispersed Ag<sup>0</sup> particles seemed to favor the greater activity at low temperature. In contrast, larger Ag<sup>0</sup> particles were related to higher N<sub>2</sub> selectivity.

When Ag/Al<sub>2</sub>O<sub>3</sub> sample was held at 160 °C for about 50 h, Ag<sup>0</sup> was only slightly oxidized (Fig. 9). However, some Ag<sup>0</sup> particles aggregated (Fig. 7b). The NH<sub>3</sub> conversion over the H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> (IM) at 160 °C did not decrease over about 50 h (Fig. 3), while the selectivity to N<sub>2</sub> increased slightly (from 46% to 50%) during this period. These results clearly indicate that Ag<sup>0</sup> is the active species in these conditions and it could be retained at 160 °C. The aggregated Ag<sup>0</sup> particles did not influence the high NH<sub>3</sub> conversion at this condition, but caused the higher N<sub>2</sub> selectivity.

Combining the cyclic test results (Fig. 4) with the TEM (Fig. 7) and UV/Vis characterizations (Fig. 9), we discovered that after 1 test cycle to 220 °C, some Ag<sup>0</sup> particles were oxidized to Ag<sup>+</sup> species and some un-oxidized Ag<sup>0</sup> particles aggregated into larger ones. After 5 test cycles, the Ag<sup>0</sup> particles left were gradually oxidized and the un-oxidized Ag<sup>0</sup> particles aggregated more obviously. The NH<sub>3</sub> conversion at low temperature (≤160 °C) decreased gradually and the N<sub>2</sub> selectivity went up significantly, which was consistent with the oxidization of Ag<sup>0</sup> and the aggregation of Ag<sup>0</sup> particles. This phenomena proves that the oxidation of Ag<sup>0</sup> resulted in the decrease of active species of Ag/Al<sub>2</sub>O<sub>3</sub> at the low temperature (≤160 °C), thus the activity decreased gradually at low temperature. On the other hand, the aggregation of the left Ag<sup>0</sup> particles on the support is another important reason for the decrease of the low temperature activity in cycle test. But the aggregated larger Ag<sup>0</sup> particles also caused the enhancement of the N<sub>2</sub> selectivity at low temperature. However, in each cycle, the NH<sub>3</sub> conversion could still achieve 100% at 220 °C, as the fresh Ag/Al<sub>2</sub>O<sub>3</sub> (IM). This indicates the Ag<sup>+</sup> could be the main active species at higher temperature and thus the high NH<sub>3</sub> conversion could be retained over the Ag/Al<sub>2</sub>O<sub>3</sub> (IM) at high temperature (>220 °C).

It was reported that the activity of NH<sub>3</sub> oxidation over Ag/Al<sub>2</sub>O<sub>3</sub> at low temperature was related to the catalyst's ability to take part in dissociative or non-dissociative adsorption of O<sub>2</sub> [2]. The molecular O<sub>2</sub> could be adsorbed dissociatively on the H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub>. In this case, catalysts IM and IW, with high surface areas and well-dispersed Ag<sup>0</sup> particles, favor the dissociative adsorption of O<sub>2</sub>. Larger Ag<sup>0</sup> particles on Ag/Al<sub>2</sub>O<sub>3</sub> (SOL) were unfavorable for the dissociative adsorption of O<sub>2</sub>, which resulted in a lower NH<sub>3</sub> conversion at low temperature. The molecular O<sub>2</sub> could hardly be adsorbed dissociatively on the fresh Ag/Al<sub>2</sub>O<sub>3</sub>. In this case, NH<sub>3</sub> mainly reacts with molecular O<sub>2</sub>. The dissociatively adsorbed oxygen might contribute to high activity for the SCO of NH<sub>3</sub> over the H<sub>2</sub> pretreated catalyst at low temperature (<140 °C). According to the results above, at higher temperature (>140 °C), Ag<sup>+</sup> could also be an active species for the activation of NH<sub>3</sub> prior to reacting with the molecular O<sub>2</sub> at higher temperature (>140 °C). The role of different O<sub>2</sub> species for the SCO of NH<sub>3</sub> and the SCO mechanism over

the fresh and H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> catalysts will be studied further in our following work.

## 5. Conclusions

On the basis of the above results, we conclude that the activity of 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalysts at different temperatures mainly relate to the states of the Ag species. Ag<sup>0</sup> is the main active species at low temperature (<140 °C). However, Ag<sup>+</sup> could also be the active species at temperatures above 140 °C. The high NH<sub>3</sub> conversion over the H<sub>2</sub> pretreated Ag/Al<sub>2</sub>O<sub>3</sub> catalyst could be maintained at 160 °C for about 50 h, because the metallic Ag<sup>0</sup> species could be retained at this condition. In contrast, the Ag<sup>0</sup> species could be oxidized to Ag<sup>+</sup> at temperatures above 160 °C.

Ag/Al<sub>2</sub>O<sub>3</sub> catalysts with high surface areas and well-dispersed Ag<sup>0</sup> particles favor greater activity at low temperature, whereas their N<sub>2</sub> selectivity is not good. A catalyst with large Ag<sup>0</sup> particles provides high N<sub>2</sub> selectivity but its activity is not good at low temperature. Both Ag particle size and the states of the Ag species are important factors that influence the activity and N<sub>2</sub> selectivity of the SCO of NH<sub>3</sub>.

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