Supporting Information

1. Experimental

1.1 Materials

TiO_2 was obtained from the Catalysis Society of Japan. The sample numbers are JRC-TIO-16 and JRC-TIO-17. JRC-TIO-16 is a TiO_2 prepared by Sakai Chemical Industry of Japan and has a rutile-type structure. The BET specific surface area upon receipt was 109 m^2 g^{-1}, and that after Ag loading and calcination was 33-37 m^2 g^{-1}. JRC-TIO-17 is the world well-known Degussa P-25 (Germany), distributed by Evonik of Japan. According to the analysis table, it consists of about 70% anatase TiO_2, 20% rutile TiO_2, and 10% amorphous TiO_2. Other oxides were purchased from reagent companies as special grade reagents and used as is in the experiments.

Silver loading on the supports was performed by a conventional impregnation method using a silver nitrate solution. The loading amounts were 0.7-5.0 wt%. Catalyst preparation by the ET method was performed as follows. Solution A was prepared by dissolving silver nitrate in ethanol, and Solution B was prepared by suspending the support in ethanol. Solution A was slowly added into Solution B heated at 70-80°C. After the addition was completed, the heating was continued until all the ethanol was evaporated. The resulting powder was dried in air at 80°C overnight. In the ND method, Solution C was prepared by dissolving a predetermined amount of neodymium oxide in a dilute aqueous nitric acid solution, and Solution D was prepared by suspending the support in water. Solution C was slowly added into Solution D heated at 70-80°C. After the addition was completed, the heating was continued and all the water was evaporated. The resulting solid was dried at 80°C overnight. In the preparation of the ND-ET catalyst, the above ET method was applied to the ND support prepared by the above method.

After the loading operation, all the catalysts were calcined in air at 500°C for 4 hours. After calcination, the solids were ground in a mortar and the granules were sized to 0.3-0.6 mm in diameter. The crystal structure of the support and the particle size of the supported Ag were measured using an X-ray diffractometer. A Bruker (USA) D2_Phaser with CuKα line and a Ni filter was used for the measurements. The BET surface areas and the BJH pore distributions were determined using adsorption-desorption isotherms of N_2 measured at the liquid nitrogen temperature.

1.2 Experimental Method

A quartz reaction tube was used for the catalytic activity measurements. The outer and inner diameters of the reaction tube are 14 and 12 mm, respectively. A thermocouple sheath tube with an outer diameter of 5 mm was placed inside the reaction tube, and the temperature of the catalyst bed was measured by a thermocouple inserted into the tube. In this experiment, the amount of catalyst was varied to change the space velocity SV of the reaction. Typical experimental conditions were a catalyst volume of 0.6 mL and a total reaction gas flow rate of 100 mL min^{-1} (SV=10,000 h^{-1}). The catalyst weight was 0.3-0.5 g (depending on the specific gravity of the support). A mixture of NO, C_3H_6, O_2, H_2O, and N_2 gas adjusted to any concentration was introduced from the top of the reaction tube. The gas leaving the reaction tube was directed to a Fourier Transform Infrared spectrometer FT-IR equipped with a 2.4 m gas cell. The FT-IR measured the NH_3 formation rate and the C_3H_6 combustion rate from the absorbance of NH_3 and C_3H_6. Ammonia yield Y_{NH3} and C_3H_6 conversion X_{C3H6} were calculated using the equations (1) and (2) in the main text.

2. Supplemental Figures

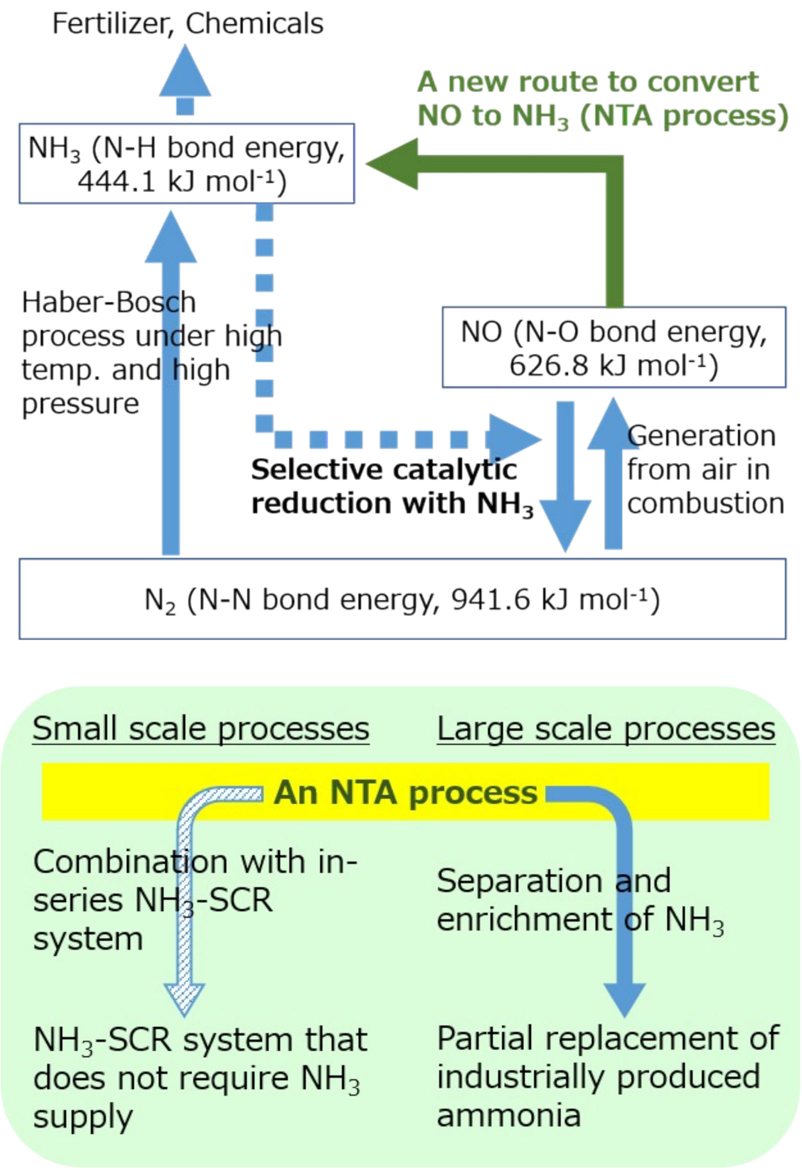


Figure S1. Current process of nitrogen cycle process and proposed new reaction pathway (NOx to Ammonia, NTA). Reproduction of Figure 1 from the previous report.[1]

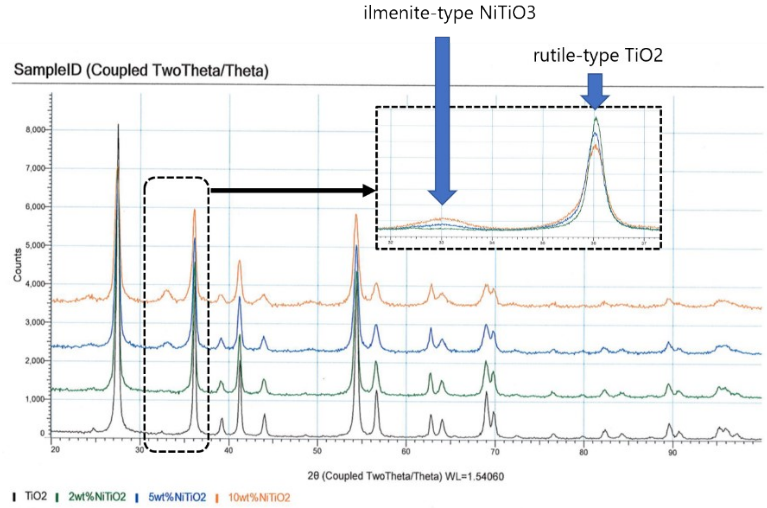


Figure S2. XRD spectra of TiO_2 catalysts loaded with 0 (black), 2 (green), 5 (blue), and 10 wt% (orange) Ni. The enlarged figure shows one of the main diffraction lines of the ilmenite-type composite oxide $NiTiO_3$ (diffraction angle 33°) and rutile-type titanium dioxide (diffraction angle 36°).

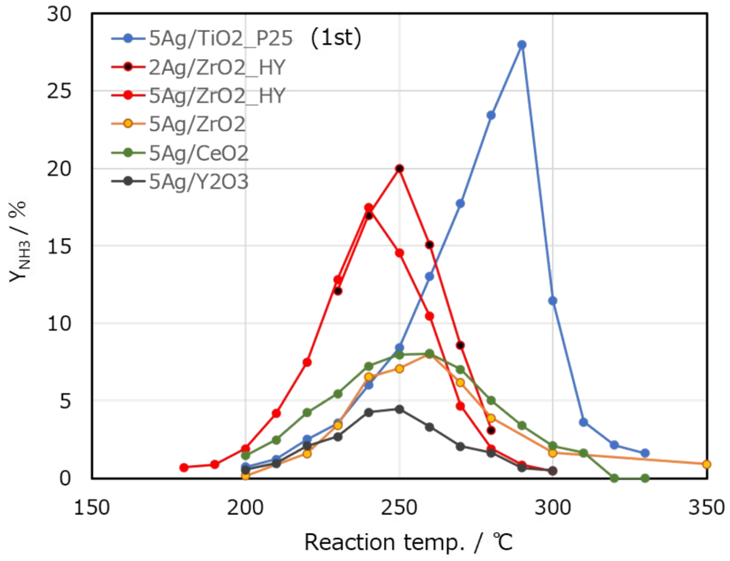


Figure S3. Change in catalytic activity of Ag with the support. All catalysts were prepared by the conventional impregnation method. ZrO_2_HY is ZrO_2 prepared with a hydration method by Daiichi Kigenso Kagaku Kogyo Co. Ltd. Japan, while ZrO_2 is an oxide purchased from Kanto Chemical. Co., Japan. The catalytic activity was measured at a catalyst volume of 0.6 mL, a total reaction gas flow rate of 100 mL/min (SV 10,000 h^{-1}), and gas partial pressures of 0.1% NO, 0.5% C_3H_6, 10% O_2, 0% H_2O, and balanced N_2.

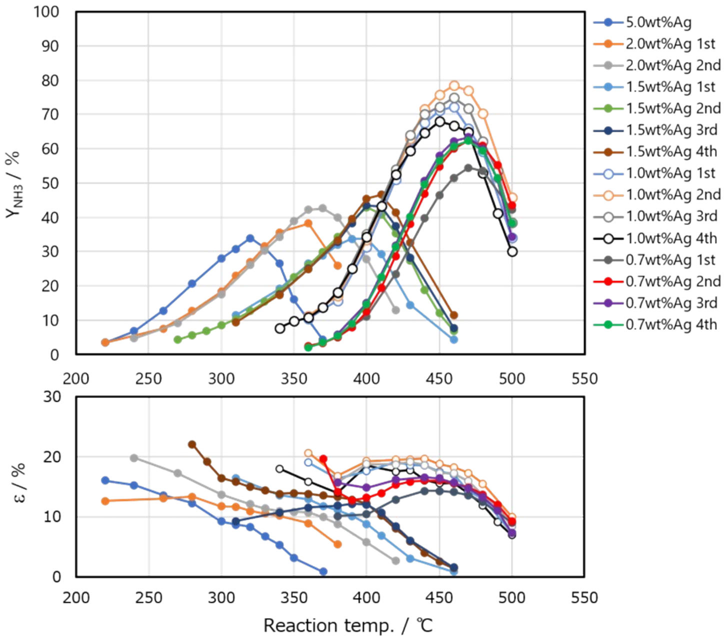


Figure S4. Dependence of the catalytic activity of Ag/TiO_2 prepared by the conventional impregnation method on the loading amount of Ag. The upper panel is a reproduction of Figure 5 in the previous report.[1] The lower panel shows effective utilization of reductant ε. The catalytic activity was measured under the standard reaction condition.

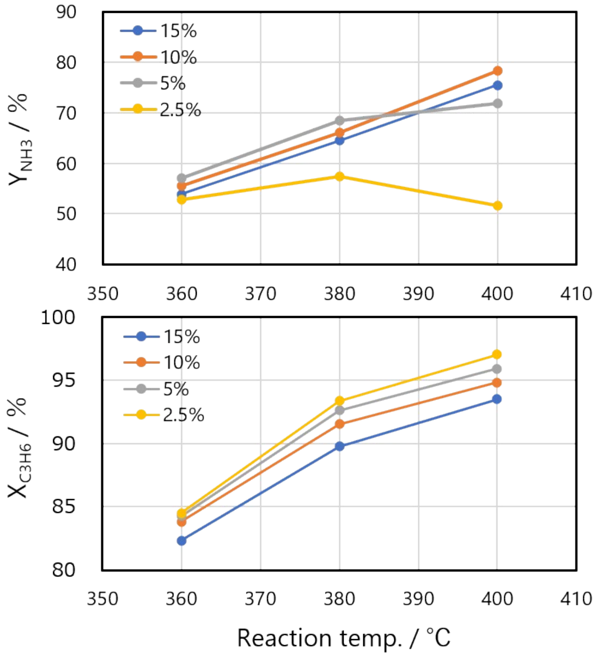


Figure S5. NH_3 yield and C_3H_6 conversion at 360-400°C on the 2.0 AgET/TiO_2 catalyst as a function of H_2O partial pressure. The catalytic activity was measured at a catalyst volume of 0.6 mL, a total reaction gas flow rate of 100 mL/min (SV 10,000 h^{-1}), and gas partial pressures of 0.1% NO, 0.5% C_3H_6, 10% O_2, 2.5-15% H_2O, and balanced N_2.

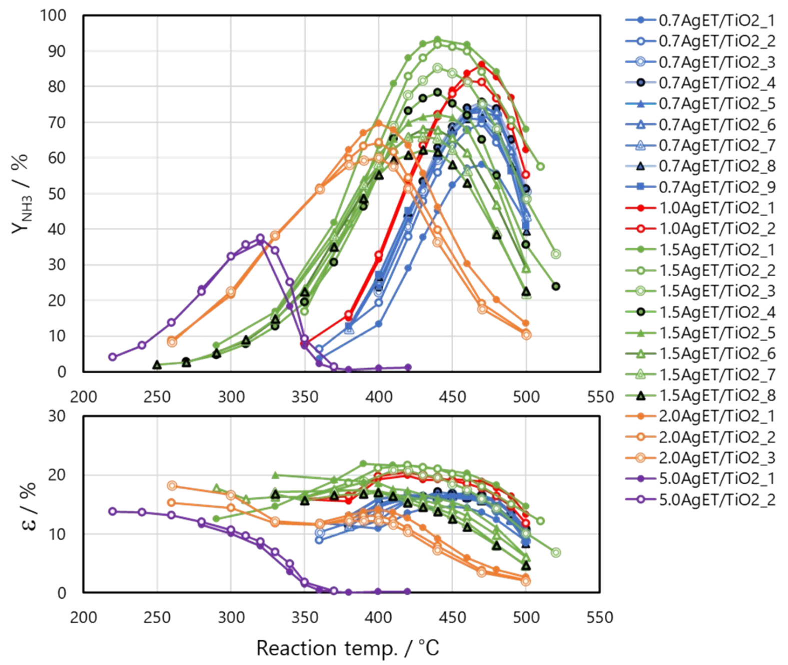


Figure S6. Catalytic activity of ET catalyst as a function of Ag loading and experimental repetition. Upper panel shows NH_3 yield and lower panel shows effective utilization of reductant ε. The last digits of the catalyst names indicate the number of repetitions. Catalytic activity was measured under the standard reaction conditions.

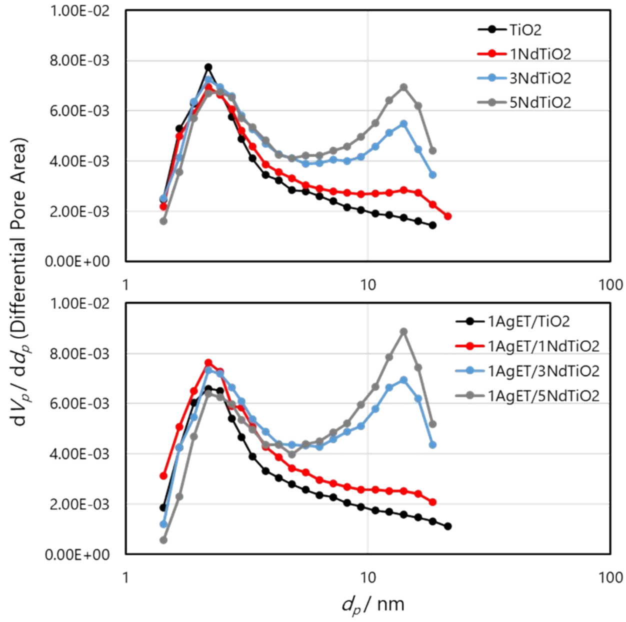


Figure S7. Change in pore size with the ND treatment. The upper panel shows the distributions of the support only (0-5NdTiO_2), and the lower panel shows those of various NdTiO_2 supported 1.0AgET catalysts. Pore sizes were calculated by the BJH method from N_2 adsorption isotherms at liquid nitrogen temperature.

3. Characterization of Ag/TiO_2 catalysts using XRD and UV-VIS measurements.

3.1 XRD measurements

In this study, we mainly used XRD and UV-VIS techniques to analyze the loading state of Ag on the catalyst. Ag was very mobile on TiO_2 as shown below, and qualitative or quantitative characterization of its properties was very difficult. We showed here only a rough trend.

First, characterization of Ag particles was performed by XRD measurement. Figure S8 shows the XRD pattern of $5Ag/TiO_2$ as a representative example, in which diffraction lines from rutile-type titanium dioxide appeared at 20-100 degrees (red vertical bars indicates the standard diffraction lines). The diffraction line of silver particles appeared around 38 degrees. Since the intensity of the Ag diffraction line was very small, the peak is enlarged in the upper right figure. The measured diffraction line is shown in black; the smoothed diffraction line is shown in red; and the diffraction line with the sub-diffraction line derived from Cu-Kα2 removed is shown in blue. In this study, the Sherrer's equation was applied to the diffraction lines to measure the silver particle size.

$$D=K\lambda/\beta\cos\theta$$

where D is the diameter of the measured particle (nm); *K is the* Scherrer constant, which was 0.89 in this study; β is the half width of the diffraction peak, corrected using the instrumental constant measured by a Si single crystal; θ is half the diffraction angle 2θ. The (111) diffraction line of silver, $2\theta = 38.1$ degrees, was used for the measurement.

The XRD patterns of catalysts prepared by the ET method are summarized in Figure S9 as an example of measurement. The upper panel shows the diffraction lines measured before the NTA reaction and the lower panel shows the diffraction lines measured after the NTA reaction. Before the reaction, weak diffraction lines appeared in the 5Ag sample, but almost no diffraction lines could be observed in the other samples; after the NTA reaction, diffraction lines were observed in all samples. The intensity of diffraction lines was small in the sample with low Ag loading. Silver particle sizes were calculated for the impregnation, ET, and ND-ET catalysts and plotted in relation to the ammonia production activity. The relationship is shown in Figure S10. In this figure, except for the bracketed plots, we believe that the correlation is like the blue straight line. That is, we believe that the smaller the silver particle size, the higher the NTA activity. Note, however, that the catalysts that could be plotted here are only those that gave silver diffraction lines after the NTA reaction. For example, the $1.0AgET/1NdTiO_2$ catalyst that gave high activity in Figure 7 is not plotted in this figure because no diffraction lines of silver particles were observed after the reaction.

We have encountered a very troubling problem in XRD measurements. An example of the results is shown in Figure S11. This figure shows the XRD patterns of a $2Ag/TiO_2$ catalyst prepared by the impregnation method. In this experiment, the catalyst was left in air after preparation, and XRD was measured as a function of the number of days left in air. It is clear that the diffraction line intensity increased and the FWHM broadened as the number of days of exposure increased; the XRD diffraction lines after 6-8 days of exposure were almost identical, indicating that the silver particles have changed almost completely within a week. The silver particle size changed from 180 nm (immediately after the preparation), 92 (2nd day), 80 (3rd day), 47 (6th day), 49 (7th day), and 49 (8th day). These results indicate that the atmosphere in which the catalyst is stored and the timing at which it is used for catalytic reactions are very important. This study has not yet reached the stage where these factors can be comprehensively examined and standard conditions can be proposed.

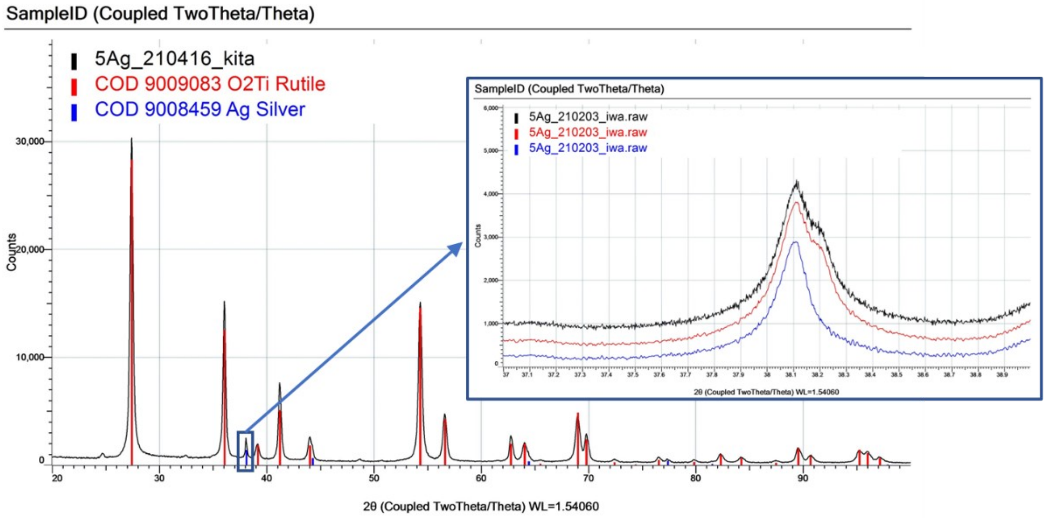


Figure S8. XRD diffraction lines of 5Ag/TiO$_2$. The (111) diffraction line of Ag is included in the enlarged figure. The black line in the enlarged figure is the measured spectrum, the red line is the spectrum with noise removal, and the blue line is the spectrum with removal of the sub-diffraction line derived from Cu Kα2.

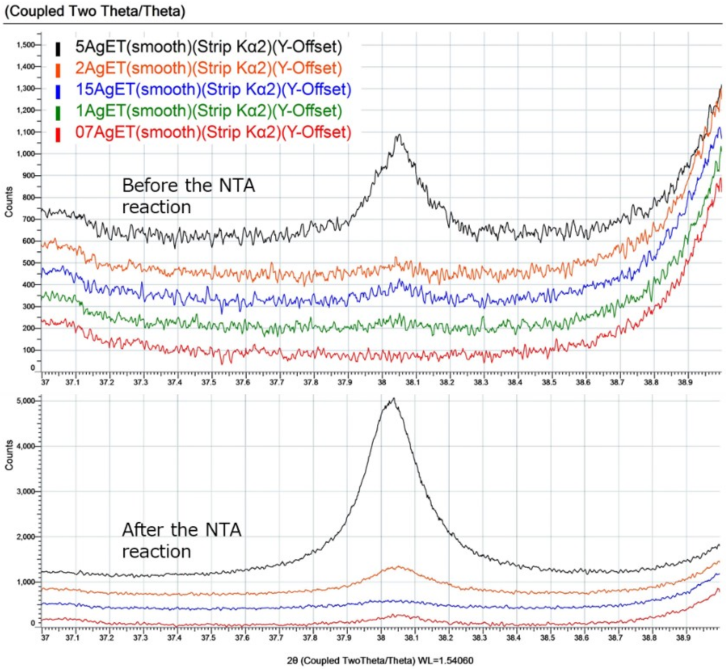


Figure S9. XRD diffraction patterns of 0.7-5AgET/TiO$_2$ catalyst before and after the NTA reaction. The upper panel shows the pattern before the NTA reaction and the lower panel shows the pattern after the reaction.

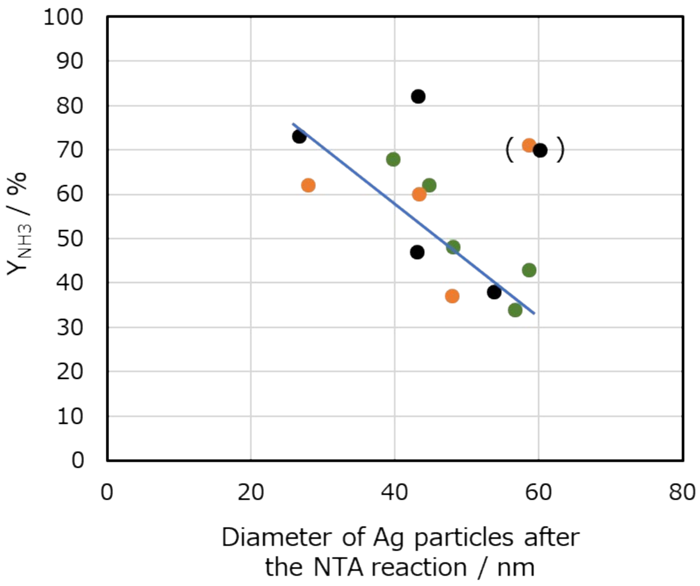


Figure S10. Relationship between silver particle size and ammonia yield. The particle size was determined from XRD diffraction patterns of catalysts after the NTA reaction. The green catalysts were prepared by the impregnation method, the orange catalysts were prepared by the ET method, and the black catalysts were prepared by the ND-ET method. Note that not all catalysts gave silver diffraction lines, so only those that could be measured are plotted in this figure.

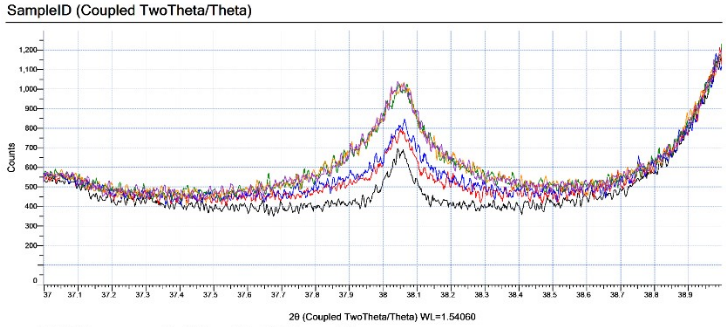


Figure S11. Changes of XRD pattern when the $2Ag/TiO_2$ catalyst is calcined at 500°C for 4h in air and then left in air at room temperature. The spectrum measured immediately after calcination is shown in black. The catalyst samples were then left in air at room temperature for 2 days (red), 3 days (blue), 6 days (green), 7 days (orange), and 8 days (purple).

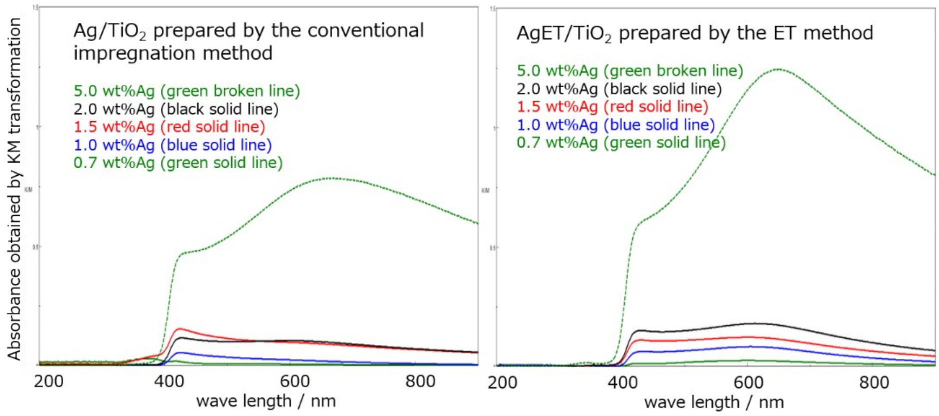
3.2 UV-VIS measurements

UV-VIS spectra based on silver plasmon absorption were observed for the Ag/TiO_2 catalyst used in this study. The results for the impregnation and ET catalysts are summarized in Figure S12. All spectra were measured immediately after the catalyst preparation. Only scattered light is observed while the silver loading is small (0.7-2.0 wt%), but at 5.0 wt% large absorption bands appear around 400 nm and 650 nm. These are attributed to the sub and main bands of plasmon absorption of silver with a particle size of 100-200 nm. It is clear from the figure that the ET catalyst gave larger peaks.

In this UV-VIS absorption bands, shape change was also observed after leaving the catalyst in air at room temperature. The changes in 2Ag/TiO_2 are summarized in Figure S13. The figure shows the results of 0-15 days change. Immediately after the preparation, only scattered light spectra were observed as already shown in Figure S12, but after 1 day, a large plasmon absorption appeared. The intensity of this plasmon absorption increased or decreased with the number of days of storage, and it will take a considerable number of days until it becomes constant (Figure S14). In addition, the position of the maximum absorption shifted gradually to the lower wavelength side (Figure S14). Previous studies reported that the shift of the maximum absorption wavelength to the shorter wavelength side corresponds to a decrease in Ag particle size. The direction of this change is the same as that observed by XRD (Figure S11), where the Ag particle size gradually decreased when the sample was left in air at room temperature. These changes were similar regardless of the silver loading method, as shown in Figure S14.

As described above, both XRD and UV-VIS measurements showed that the silver particle size gradually decreases when left in air at room temperature. Although we have yet to quantitatively measure this change, it may be possible to further improve NTA activity by using it as a catalyst at the appropriate time.

Figure S12. UV-VIS spectra of Ag/TiO_2 prepared by the impregnation method (left) and the ET method (right). All spectra were recorded in air at room temperature using an integrating sphere. The reference plate in the measurement was TiO_2.



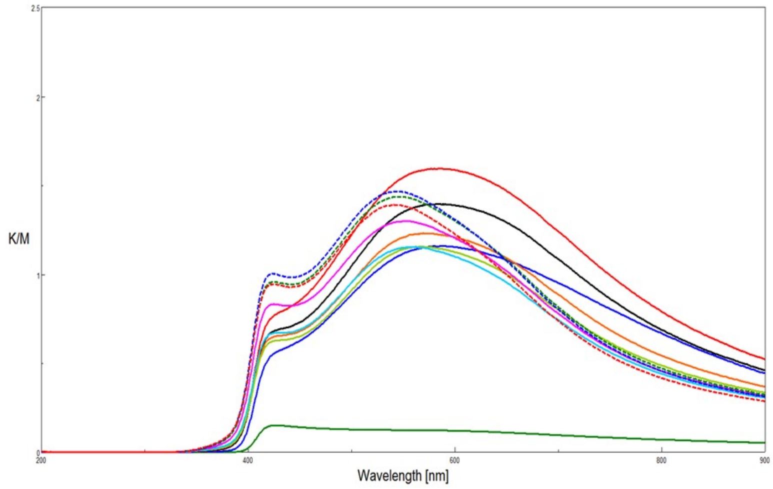


Figure S13. Change in UV-VIS spectra of $2Ag/TiO_2$ catalyst after calcination at 500°C for 4h in air and then left in air at room temperature. The measurement method is the same as in Figure S12. The numbers of days elapsed were as follows.

Green: immediately after the preparation. Blue: after 1 day. Red: after 4 days. Black: after 5 days. Orange: after 7 days. Yellow-green: after 8 days. Light blue: after 11 days. Pink: after 12 days. Green (dotted line): after 13 days. Blue (dotted line): after 14 days. Red (dotted line): after 15 days.

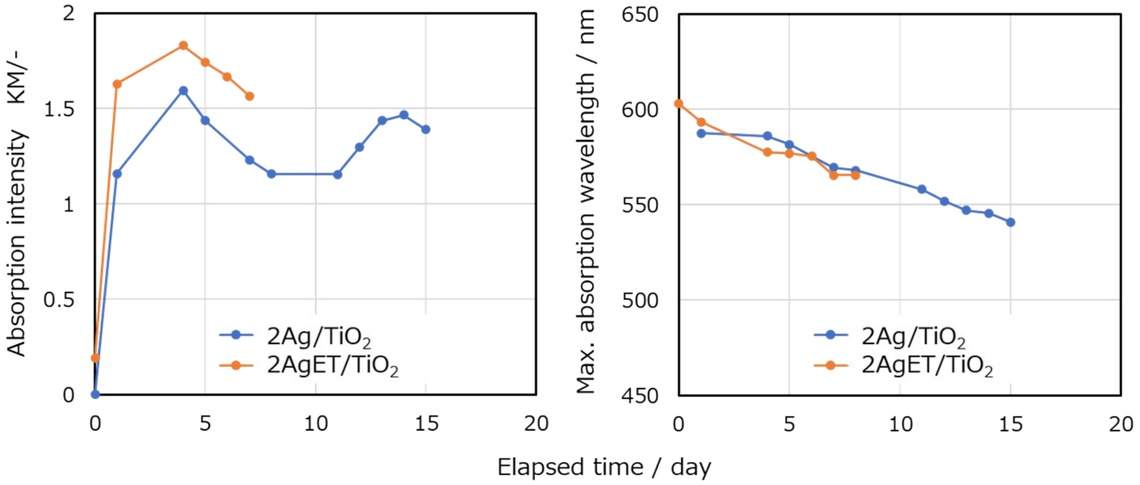


Figure S14. Change in the intensity and wavelength of absorption maxima when the samples, $2Ag/TiO_2$ and $2AgET/TiO_2$, were left in air at room temperature. The measurement method is the same as in Figure S12.