1. Introduction

There have been many power plants in Japan that use fossil fuels including coal, petroleum and natural gas. Coal-fired power plants have been used because of the low cost of coal and stability of its supply, though the use of coal-fired power plants has been gradually decreasing in order to reduce the production of greenhouse gases and related pollutants. The number of harmful products generated from the combustion process must be reduced as much as possible to deal with the problem of greenhouse gases. Particulate matter, sulfur oxide (SO\textsubscript{x}) and nitrogen oxide (NO\textsubscript{x}) are the main pollutants produced from power plants and boilers, and the ratios of these pollutants vary depending on the kind of combusted fuel\textsuperscript{1-2}. NO\textsubscript{x} can cause acid rain, respiratory disorders and photochemical smog, for which effective countermeasures are needed\textsuperscript{3-5}. Selective catalytic reduction (SCR) using is the main reaction used in a current power plant systems for elimination of NO\textsubscript{x}. The reaction proceeds as follows\textsuperscript{6-8}:

\begin{align*}
4\text{NO} + 4\text{NH}_3 + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 & \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} \\
\text{NO} + \text{NO}_2 + 2\text{NH}_3 & \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}
\end{align*}

Reaction (1) is a standard SCR reaction, while (2) and (3) are slow and fast SCR reactions, respectively. The reactions (2) and (3) proceed as NO is oxidized to NO\textsubscript{2}. The reactions produce harmless N\textsubscript{2} and water from NH\textsubscript{3}, oxygen, and NO\textsubscript{x}. During NH\textsubscript{3}-SCR, the oxidation of the reducing agent NH\textsubscript{3} can result in the production of NO and N\textsubscript{2}O and can reduce the efficiency of NH\textsubscript{3}-SCR\textsuperscript{7}. Furthermore, in the case of combusting fuels that contain sulfur, SO\textsubscript{2} is generated at a high reaction temperature and is oxidized to SO\textsubscript{3} followed by reaction with NH\textsubscript{3}\textsuperscript{9,10}. These reactions result in

\begin{align*}
4\text{NO} + 4\text{NH}_3 + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 & \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} \\
\text{NO} + \text{NO}_2 + 2\text{NH}_3 & \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}
\end{align*}
the production of ammonium sulfate on the surface of the catalysts, which can be catalyst poisoning. Therefore, suppression of these side reactions is important in addition to improvement of NH3-SCR. In addition to these chemically deactivating factors, produced dust also causes the deposition on catalysts and physical clogging\textsuperscript{10,11}. The SCR system is generally placed just after the boiler followed by the electric precipitator and the deSO\textsubscript{2} system\textsuperscript{12}. Because of this order, the SCR catalyst is directly exposed to untreated dust and SO\textsubscript{x}, and the life of catalyst is shortened. This problem could be solved if the SCR catalyst is placed at the end of the system. However, another heat exchanger would be required to reheat the exhaust gas to an active temperature of the SCR catalyst because the temperature of the gas would be decreased at the end part. Therefore, the development of a NH3-SCR catalyst that works at a lower temperature would contribute to the establishment of a new SCR process without the need to place another apparatus.

Zeolite (Cu-ZSM5, Fe-ZSM5, etc.) and TiO\textsubscript{2}-supported V\textsubscript{2}O\textsubscript{5} and WO\textsubscript{3} (V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}, WO\textsubscript{3}/TiO\textsubscript{2}, and V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2}) have been widely used as commercial catalysts of NH3-SCR\textsuperscript{12-20}. A zeolite catalyst has stability even at 600 °C and can be used in a high-temperature environment\textsuperscript{13-16}. TiO\textsubscript{2}-supported V\textsubscript{2}O\textsubscript{5} and WO\textsubscript{3} catalysts are generally used as NH3-SCR catalysts for power plants because TiO\textsubscript{2} has little activity for oxidation of SO\textsubscript{2} and because of its chemical stability\textsuperscript{12,17-20}. Vanadium oxide is an active component of NH3-SCR, but it has activity for oxidation of SO\textsubscript{2} to SO\textsubscript{3}\textsuperscript{9,10}. Therefore, the loading amount of vanadium oxide is limited to below 1 wt% in order to suppress the further oxidation of SO\textsubscript{2}. Tungsten oxide also contributes as a co-catalyst to thermostability and is generally supported with a loading amount of 10 wt%\textsuperscript{12}.

Although many NH3-SCR catalysts that can be used over a wide temperature range have been investigated, the development of a practical catalyst that works at low temperature (\textless 200 °C) is still challenging. A recent study has shown that deposition of precious metals, such as Pt, Rh and Pd, promotes NH3-SCR activity at a low temperature, though noble metal catalysts have the potential to produce N\textsubscript{2}O by NH3 oxidation\textsuperscript{21,8}. Gold, another precious metal, has also been reported as a catalyst for elimination of NO\textsubscript{x}, and previous works showed that gold works as an active species of hydrocarbon-selective catalytic reduction (HC-SCR)\textsuperscript{3,12,21,22}, though the effect of gold on NH3-SCR is unclear. In this work, we investigated the NH3-SCR activities of metal oxide-supported gold nanoparticle (NP) catalysts at low temperatures (\textless 200 °C), and we investigated the effects of reaction temperature on products and side reactions (Fig. 1).
CuO powder was added to an aqueous solution of (NH₄)₂PdCl₄ and H₂PtCl₆ to be 1 wt%, respectively. Next, the resulting dispersion was heated to make the water evaporate (120 °C), and the resulting powder was dried in air (120 °C, overnight). Then the dried powder was calcined in air (400 °C, 3 h). Finally, the air-calcined powder was treated under an H₂/N₂ stream (vol/vol = 5/45, 300 °C, 2 h).

2.4. Binary Metal Oxide Supported Gold Catalyst (Au/CuO/TiO₂ and Au/CuO/Al₂O₃)

Binary metal oxide-supported gold catalysts were synthesized by combining the impregnation and deposition-precipitation methods to support copper and gold on another metal oxide support. Cu(NO₃)₂·3H₂O was added to the minimum amount of water that can completely dissolve Cu(NO₃)₂·3H₂O. Next Al₂O₃ powder and TiO₂ powder were added to the solution to the desired loading amount. Then the resulting dispersion was heated to make water evaporate (120 °C), and the resulting powder was dried in vacuum overnight. Finally, the dried powder was calcined in air (300 °C, 4 h). Gold was supported on the resulting Cu/TiO₂ powder and Cu/Al₂O₃ powder by the same procedure that described in section 2.2.

2.5. Catalytic Test

NH₃-SCR, NO oxidation, and NH₃ oxidation activity were investigated using a fixed-bed flow reactor. An NOx analyzer (Testo-350, Testo SE & Co. KGaA) and a Fourier transform infrared (FT-IR) spectrometer equipped with a 2.3-L gas cell (FT-IR-4700, JASCO Corp.) were used for analysis of outlet gas. Each catalytic parameter was calculated as follows:

\[
\text{NO conversion} \% = \frac{\text{NO}_\text{in} - \text{NO}_\text{out}}{\text{NO}_\text{in}} \times 100 \quad (4)
\]

\[
\text{N}_2 \text{ selectivity} \% = \frac{2 \times \text{N}_2\text{out}}{(\text{NO}_\text{in} + \text{NH}_3\text{in}) - (\text{NO}_\text{out} + \text{NH}_3\text{out})} \times 100 \quad (5)
\]

\[
(2 \times \text{N}_2\text{out} = (\text{NO}_\text{in} + \text{NH}_3\text{in}) - (\text{NO}_\text{out} + \text{NH}_3\text{out} + \text{NO}_\text{2out} + 2 \times \text{N}_2\text{O}_\text{out}))
\]

\[
\text{N}_2 \text{ yield} \% = \frac{\text{NO conversion} \times \text{N}_2 \text{ selectivity}}{100} \quad (6)
\]

\[
\text{NO}_2 \text{ selectivity} \% = \frac{\text{NO}_\text{2out}}{\text{NO}_\text{in} - \text{NO}_\text{out}} \times 100 \quad (7)
\]

\[
\text{NH}_3 \text{ conversion} \% = \frac{\text{NH}_3\text{in} - \text{NH}_3\text{out}}{\text{NH}_3\text{in}} \times 100 \quad (8)
\]

\[
\text{NO selectivity} \% = \frac{\text{NO}_\text{out}}{\text{NH}_3\text{in} - \text{NH}_3\text{out}} \times 100 \quad (9)
\]

\[
\text{N}_2\text{O selectivity} \% = \frac{\text{N}_2\text{O}_\text{out}}{\text{NH}_3\text{in} - \text{NH}_3\text{out}} \times 100 \quad (10)
\]

3. Results and Discussion

3.1. Effect of Support of Gold on NH₃-SCR

First, we performed screening of gold NPs supported on a metal oxide (Au/NOx, 1 wt%) at 200 °C to consider the effect of support on NH₃-SCR (Fig. 2(a)). All of the catalysts showed an increase in NO conversion after deposition of gold on the metal oxide supports compared to NO conversion with only support materials. Although Al₂O₃ and TiO₂ themselves had no activity, the reaction proceeded by loading gold on these supports. Since MnO₂, Fe₂O₃, NiO, and Co₃O₄ themselves act as active species of NH₃-SCR⁸,25,27, the

(a) Reaction conditions: temperature, 200 °C; catalyst, 0.750 g; total flow rate, 500 mL min⁻¹ (NO 440 ppm, NH₃ 440 ppm, O₂ 4 vol%, Ar balance); time on stream, 0.5 h; analytical instrument, NOx analyzer.

(b) Reaction conditions: temperature, 200 °C; catalyst, 0.750 g; total flow rate, 500 mL min⁻¹ (NO 250 ppm, NH₃ 250 ppm, O₂ 4 vol%, Ar balance); time on stream, 0.5 h; analytical instrument, FT-IR.

Fig. 2 (a) Effect of Metal Oxide Support of Gold NP (1 wt%) on NO Conversion, and (b) N₂ Selectivity of Gold NP (1 wt%) Supported on a Metal Oxide as a Function of NO Conversion.
values of NO conversion were calculated to be 79, 39, 70 and 37 %, respectively. The activities of Au/Fe2O3 and Au/NiO were increased compared to those of only the corresponding metal oxide supports, although Au/MnO2 showed almost the same NO conversion as that of only MnO2. It is assumed that the contribution of MnO2 to NH3-SCR overcomes the effect of depositing gold. The effects of deposition of gold were notable for ZrO2 and CeO2: the NO conversion rates of ZrO2 and CeO2 were less than 30 %, while Au/ZrO2 and Au/CeO2 showed NO conversion of 94 % and 97 %, respectively.

We also measured the N2 selectivity of Au/MO catalysts at 200 °C to consider the products (Fig. 2(b)). N2 selectivity of Au/MO catalysts ranged from 0 to 38 %, indicating that another side reaction could proceed at 200 °C. The order of N2 selectivity of Au/MO catalysts had no relationship to NO conversion. Au/CeO2 showed the largest rate of NO conversion (97 %), while N2 selectivity was determined to be 23 %. NH3-SCR of Au/TiO2 and Au/ZrO2, the NO conversion rates of which were almost 100 %, could also proceed with side reaction. Au/CuO exhibited the highest N2 selectivity (38 %) and a relatively high rate of NO conversion (85 %). Thus, another side reaction can proceed at 200 °C in the case of using gold catalysts although NH3-SCR proceeds simultaneously. Based on these results, we focused on a NH3-SCR of Au/CuO, which showed the highest N2 selectivity at 200 °C, and performed further investigation of the activity of NH3-SCR at temperatures below 200 °C.

3.2. NH3-SCR of Au/CuO
The temperature dependence (100-200 °C) of 1 wt% Au/CuO and that of only CuO support on NH3-SCR were determined to consider the selectivity and the products at low temperatures. At all of the temperatures, 1 wt% Au/CuO had a higher rate of NO conversion than that of only CuO (Fig. 3(a), red and blue lines, respectively). On the other hand, the N2 selectivity of 1 wt% Au/CuO decreased with increasing tem-
perature and was less than 50 % at temperatures above 150 °C, while CuO showed the N₂ selectivity of 90 % even at 200 °C (Fig. 3(b), red and blue lines, respectively). At temperatures above 150 °C, the yield of N₂ was also higher with CuO than with 1 wt% Au/CuO (Fig. 3(e), red and blue lines, respectively). The results indicate that NH₁-SCR proceeds at temperatures above 150 °C with only CuO but that 1 wt% Au/CuO causes another side reaction in addition. In contrast to the results for NH₂-SCR at high temperatures (150 °C <), N₂ yield of 1 wt% Au/CuO was greater than that of CuO at temperature below 120°C. At 100 °C, although NO conversion and N₂ yield were around 20 %, N₂ selectivity was almost 100 %, indicating that only of NH₁-SCR proceeds. We also monitored the gas concentration of N₂O of 1 wt% Au/CuO and CuO, and we found that 1 wt% Au/CuO starts to produce N₂O at around 120 °C and that the concentration significantly increases with increase in temperature (Fig. 3(d), red and blue lines, respectively). The results suggested that 1 wt% Au/CuO is favorable for NH₂-SCR to proceed at a low temperature (< 120°C), although N₂ yield and N₂ selectivity decrease at temperature above 150 °C because of the production of N₂O.

We also investigated the effect of the loading amount of gold (0.1, 0.5 and 1.0 wt%) on NH₁-SCR activity. The rate of NO conversion decreased with reduction in the loading amount of gold on CuO (Fig. 3(a)). At temperature above 150 °C, the addition of gold resulted in decrease in N₂ selectivity and N₂ yield (Figs. 3(b) and 3(c)). On the other hand, at temperature below 120 °C, all of the Au/CuO catalysts showed higher NO conversion rate and N₂ yield than those with only CuO. The 0.1 wt% Au/CuO catalyst showed N₂ selectivity of ca. 100 % at temperatures from 100 to 150 °C and the highest N₂ yield at 100 °C (Figs. 3(b) and 3(c)). These results suggest that deposition of only 0.1 wt% gold sufficiently increases the activity compared to that of only CuO at low temperatures (100-120 °C). It should be noted that N₂O was increasingly produced (Fig. 3(d)) and that N₂ selectivity and N₂ yield drastically decreased at high reaction temperature (e.g. 200 °C) when more than 0.5 wt% of gold was deposited, although there was little difference between the activity of 0.1 wt% Au/CuO and CuO. It is assumed that gold forms small clusters or exists as single atoms on the support when the loading amount is small (0.1 wt%), while deposition of a larger gold content results in the formation of three-dimensional nanoparticles\(^{28,29}\). The differences between the N₂ selectivity and between the N₂ yields at a high reaction temperature between 0.1 wt% and 0.5-1.0 wt% Au/CuO may reflect the change in the structural properties of gold on the support: gold nanoparticles, but not single atoms or tiny clusters, might catalyze the side reaction which produces N₂O. The results indicate that the deposition of gold onto CuO decreases N₂ selectivity at a high reaction temperature but increases the N₂ yield at a low reaction temperature.

### 3.3. Side Reactions of NH₃-SCR Catalyzed by Au/CuO: NO and NH₃ Oxidation

The results described above suggested the progress of a side reaction at a high reaction temperature. Although N₂O was dominantly produced as the by-product, oxidation of NO to NO₂ possibly occurs during NH₃-SCR in addition to NH₃ oxidation because metal oxide-supported gold has potential as an oxidation catalyst. There is also the possibility that the coexistence of NO and NO₂ oxidized by Au/CuO causes a fast SCR reaction (Eq. (3)) in addition to a standard SCR reaction (Eq. (1)). Hence, we measured the activities of Au/CuO and CuO for oxidation of NO and NH₃ to consider side reactions at a higher temperature. The oxidation of NO gives NO₂ as following reaction\(^{(50)}\):

\[
2NO + O₂ \rightarrow 2NO₂
\] (11)

The NO conversion and NO₂ selectivity of the NO oxidation reaction were almost the same in the case of Au/CuO and CuO (about 20 % and 100 %, respectively, Fig. 4(a)), indicating that the deposition of gold does not cause any difference in the NO oxidation reaction and that the production of NO₂ comes from the CuO support. Production of NO₂ was not observed during NH₃-SCR, meaning that NO₂ could be produced but be used as a reactant in the catalytic cycle using fast SCR reaction (Eq. (3)). Therefore, the difference between the NH₃-SCR activities of Au/CuO and CuO, especially at a low temperature, is not due to an increase in the ratio of fast SCR reaction to entire reactions since there was no difference in the amounts of NO₂ produced from Au/CuO and CuO and the NO oxidation activity was not high even at 200 °C (< 20 %).

On the other hand, there was a difference between NH₃ oxidation activities of Au/CuO and CuO (Fig. 4(b)). Possible products from the oxidation of NH₃ are NO, N₂ and N₂O, and the reaction proceeds as follows\(^{(21,27,31)}\):

\[
4NH₃ + 5O₂ \rightarrow 4NO + 6H₂O
\] (12)
\[
4NH₃ + 3O₂ \rightarrow 2N₂ + 6H₂O
\] (13)
\[
2NH₃ + 2O₂ \rightarrow N₂O + 3H₂O
\] (14)

With the existence of NO, the NH₃ oxidation reaction can also occur:

\[
4NH₃ + 4NO + 3O₂ \rightarrow 4N₂O + 6H₂O
\] (15)

In the case of only CuO, NH₃ conversion and N₂ selectivity were determined to be 30 % and 94 %, respectively, indicating that N₂ was mostly produced. We also found that CuO showed slight NO selectivity (6 %). CuO did not produce N₂O in the NH₃ oxidation but did in the case of NH₃-SCR, especially at a high temperature, as shown above (Fig. 3(d), blue...
The results indicate that the production of N\textsubscript{2}O is likely to proceed by Eq. (15), not by Eq. (14). On the other hand, Au/CuO showed an increase in NH\textsubscript{3} conversion (80\%), and N\textsubscript{2} selectivity of Au/CuO was decreased compared to that of only CuO (60\%). In addition, although production of NO was not observed, N\textsubscript{2}O selectivity of Au/CuO was determined to be 35\%, whereas it was almost 0\% in the case of only CuO. These results indicate that deposition of gold enhances NH\textsubscript{3} oxidation and produces N\textsubscript{2}O as a by-product, which is assumed to be produced by Eq. (15) in addition to Eq. (14) during NH\textsubscript{3}-SCR at a high reaction temperature, and the oxidation is gradually suppressed with decrease in reaction temperature. Based on these results, the decrease in N\textsubscript{2} selectivity and the production of N\textsubscript{2}O of Au/CuO during NH\textsubscript{3}-SCR shown in Figs. 3(b) and 3(d) can be caused by the NH\textsubscript{3} oxidation. The interface between gold nanoparticles and the metal oxide support has been thought to be the activation site of catalytic oxidation reaction and to contribute to the generation of active oxygen species\textsuperscript{32,33}. It is therefore assumed that the oxidation ability of Au/CuO is too strong and can lead to the oxidation of NH\textsubscript{3} at a high reaction temperature. Thus, at a high reaction temperature, the oxidation of NH\textsubscript{3} reduces the efficiency of NH\textsubscript{3}-SCR.

3.4. Reaction Mechanism of NH\textsubscript{3}-SCR Catalyzed by Au/CuO

The increase in NH\textsubscript{3}-SCR activity at a low reaction temperature is thought to be due to the effect of gold since there was no or little production of N\textsubscript{2}O both in the case of Au/CuO and in the case of CuO. The difference between the NH\textsubscript{3}-SCR activities of Au/CuO and CuO can be explained by the following possible reaction mechanism (Fig. 5). NH\textsubscript{3}-SCR on CuO is assumed to proceed via the reaction of adsorbed NH\textsubscript{3} on Lewis or Brønsted acid sites of the surface (NH\textsubscript{3}\textsubscript{ads}) and gaseous NO (NO\textsubscript{gas}) to produce N\textsubscript{2} and H\textsubscript{2}O followed by reduction of the surface (path 1) since the adsorption ability of NO on a metal oxide could be weak\textsuperscript{19}. Then the reduced surface is oxidized by oxygen to recover. On the other hand, it has been reported that low coordinated gold such as exposed gold atoms of high miller index crystal planes has the potential to adsorb NO\textsuperscript{22,34,36}. Nanoparticulate gold might have many coordinatively unsaturated sites compared to those of an ordered crystal. Therefore, NH\textsubscript{3}-SCR on Au/CuO might proceed by the reaction of adsorbed NH\textsubscript{3} on the support (NH\textsubscript{3}\textsubscript{ads}) and adsorbed NO (NO\textsubscript{ads}) on gold to produce N\textsubscript{2} and H\textsubscript{2}O (path 2). Then reduc-
tion and oxidation of the surface proceed as they do on only CuO. It is assumed that NH$_3$-SCR by Au/CuO proceeds via both path 1 and path 2, although the reaction of CuO utilizes only path 2, and path 1 is more favorable than path 2 at a low reaction temperature.

3.5. NH$_3$-SCR Activity of CuO-supported Precious Metal Catalysts

We also measured the NH$_3$-SCR activity of Pt and Pd NPs supported on CuO (1 wt%) in addition to gold to elucidate the effects of precious metals. A previous work showed that deposition of Pt and Pd on zeolite (Fe-ZSM5) leads to a decrease in the active temperature and that Pt has much higher activity than that of Pd. Au/CuO showed higher rates of NO conversion than those of Pt/CuO and Pd/CuO at all temperatures (Fig. 6(a)), while N$_2$ selectivity of Au/CuO was lower than that of the other catalysts (Fig. 6(b)). These results also suggested that NH$_3$ oxidation begins at a lower temperature in the case of Au/CuO and that the NH$_3$ oxidation activity of Au/CuO is stronger than that of Pt/CuO and Pd/CuO, which do not activate oxygen at the interface between the metal and support. However, the N$_2$ yield of Au/CuO was much higher than that of Pt/CuO and Pd/CuO at 100 °C (Fig. 6(c)), at which oxidation of NH$_3$ does not occur based on the results shown above (Fig. 3(d)). NO conversion and N$_2$ yield of Pt/CuO were almost the same as those of CuO at temperatures from 100 to 180 °C but were slightly increased at 200 °C. The results suggested that NH$_3$-SCR starts at a temperature around 200 °C in the case of Pt/CuO. There was no significant difference between the NH$_3$-SCR activities of Pd/CuO and CuO, indicating that the addition of Pd does not affect NH$_3$-SCR in this temperature range (100-200 °C).
has been reported that Pd and Pt also adsorb NO as well as Au \(^{37}\). Assuming that the addition of a precious metal contributes to the reaction mediated by the adsorption of NO as shown before (Fig. 5, path 2), the adsorption ability of NO on Au, Pd and Pt is crucial for the reaction to proceed the reaction. The order of NO adsorption energy has been reported to be Pd < Au < Pt \(^{38,39}\). Based on the results of this study and the reported order, Pd has weak ability for adsorption to NO, and it is assumed that there was less contribution of path 2. On the other hand, the adsorption ability of Pt is relatively strong to provide NO to NH\(_3\). Consequently, the active temperature of NH\(_3\)-SCR was higher in the case of Pt than in the case of Au. We predicted that there would be a volcano-type plot with respect to the NH\(_3\)-SCR mediated by precious metals.

**3.6. NH\(_3\)-SCR Activity of Binary Metal Oxide-supported Au NPs**

For further improvement of catalysts, we considered binary metal oxide-supported gold catalysts. We deposited CuO on Al\(_2\)O\(_3\) and TiO\(_2\) (5 wt% and 10 wt%) followed by further deposition of gold (1 wt%) onto the binary metal oxide supports. The addition of Al\(_2\)O\(_3\) and TiO\(_2\) to CuO increased the NO conversion compared to that with the Au/CuO system (Fig. 7). Au/10 wt%CuO/Al\(_2\)O\(_3\) showed the largest N\(_2\) yield (45 %), though Au/CuO exhibited the highest N\(_2\) selectivity (87 %). Au/TiO\(_2\) and Au/Al\(_2\)O\(_3\), which do not have CuO, did not show significant NH\(_3\)-SCR activity. Mixing different supports can contribute to modification of the nature of the surface, especially surface Lewis or Brønsted acidity, which is an important factor for NH\(_3\)-SCR to proceed in terms of adsorption of NH\(_3\). In addition, the interface structure between gold nanoparticles and the support, which was shown in this work to affects the NH\(_3\) oxidation ability, and the electronic state of gold also change depending on the kind of support. Although these results suggest changes in these factors, detailed effects such as the interfaces between different supports and other local structures of the surface were not able to be clarified in this work. To fully understand the results obtained for the binary metal oxide system systematically, we should further characterize the local structure of the surface in detail.

**4. Summary**

In summary, we investigated the NH\(_3\)-SCR activities of metal oxide-supported gold catalysts with the aim of the development of catalyst that works at a low temperature (< 200 °C). Au/CuO showed better activity at 200 °C than that of other metal oxide-supported gold catalysts, although production of N\(_2\)O as a by-product caused by NH\(_3\) oxidation was observed (NO conversion = 85 %, N\(_2\) selectivity = 38 %). At low reaction temperatures (100-120 °C), Au/CuO showed NH\(_3\)-SCR activity with less production of N\(_2\)O. At 100 °C, Au/CuO showed NH\(_3\)-SCR without any production of N\(_2\)O (NO conversion = 20 %, N\(_2\) selectivity = ca. 100 %). We
also found that deposition of 0.1 wt% of gold on CuO is sufficient for NH3-SCR to proceed and that further deposition induces NH3 oxidation at a high reaction temperature. The difference between the NH3-SCR activities of Au/CuO and CuO was assumed to be because the reaction mechanism of Au/CuO might involve the adsorption of NO on gold, which is more favorable than the reaction path with no adsorption of NO. Although we also tested the NH3-SCR activities of Pt/CuO and Pd/CuO, Au/CuO showed higher activity than the activities of these catalysts, which we assumed was due to differences in the NO adsorption abilities of precious metal species. The NH3-SCR activity of binary metal oxide-supported Au NPs was also investigated. At 120 °C, Au/CuO exhibited the highest N2 selectivity (87%), while Au10 wt%CuO/Al2O3 showed the largest N2 yield (45%) because of the introduction of other metal oxide species to CuO.

Gold-based catalysts have the potential to catalyze NH3-SCR at low temperatures, though the side reactions are a problem. The next tasks that we have to deal with are (1) further increase in the activity at 100 °C, (2) suppression of side reactions and (3) elucidation of the local structure around the gold-metal oxide interface. We believe that a gold catalyst, which shows not only NH3-SCR activity but also activities for other types of environment catalysis such as CO oxidation, decomposition of volatile organic compounds (VOCs)32),33),40),41), will contribute to the suppression of various pollutants including NO, by its specific catalytic nature.

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要 旨

金属酸化物担持金ナノ粒子が示す低温度NH₃-SCR活性

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石炭火力発電所あるいは工場用ボイラーでの燃焼活動によって生成する窒素酸化物（NOₓ）の効率的な除去が望まれている。そのため、当研究課題として金ナノ粒子を担持したNH₃-SCR（Selective Catalytic Reduction）が挙げられるが、低温で活性を示す实用触媒の開発が急務の課題となっている。本研究では、金属酸化物担持金ナノ粒子の低温触媒性能としての可能性を検討した。様々な金属酸化物に担持した金ナノ粒子のNH₃-SCRを検討したところ、1 wt%Au/CuO が100 ℃で NO 転化率20 %、NOx 処理率約100 %を示すことが明らかとなった。一方、200 ℃では金を担持することで起こるアンモニア分解反応に起因し、副生成物として N₂O が生成することが明らかとなった。他に、貴金属担持触媒（Pt/CuO, Pd/CuO）についても同様に活性検討を行ったが、低温（100 ~ 120 ℃）では Au/CuO が最も高い活性を示した。さらに、2元金属酸化物担持金ナノ粒子触媒のNH₃-SCRを検討し、1 wt%Au/10 wt%CuO/Al₂O₃が最も高い NOx 収率（45 %）を示すことが明らかとなった。