Nanometric Iridium Overlayer Catalysts for High-Turnover NH₃ Oxidation with Suppressed N₂O Formation

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ABSTRACT: In the present study, we prepared a 12 nm thick Ir overlayer via pulsed cathodic arc plasma deposition on a 50 μm thick Fe−Cr−Al metal (SUS) foil. Using this thin-film catalyst made NH₃ oxidation reactions more environmentally benign due to a much lower selectivity for undesirable N₂O (<5%) than that of a Pt overlayer (~70%) at 225 °C. Despite its small surface area, Ir/SUS exhibited promising activity as an ammonia slip catalyst according to a turnover frequency (TOF) >70-fold greater than that observed with conventional Ir nanoparticle catalysts supported on γ-Al₂O₃. We found that the high-TOF NH₃ oxidation was associated with the stability of the metallic Ir surface against oxidation by excess O₂ present in simulated diesel exhaust. Additionally, we found that the Ir overlayer structure was thermally unstable at reaction temperatures ≥400 °C and at which point the Ir surface coverage dropped significantly; however, thermal deterioration was substantially mitigated by inserting a 250 nm thick Zr buffer layer between the Ir overlayer and the SUS foil substrate (Ir/Zr/SUS). Although N₂O formation was suppressed by NH₃ oxidation over Ir/Zr/SUS, other undesired byproducts (i.e., NO and NO₂) were readily converted to N₂ by coupling with a V₂O₅−WO₃/TiO₂ catalyst in a second reactor for selective catalytic reduction by NH₃. These results demonstrated that this tandem reactor configuration converted NH₃ to N₂ with nearly complete selectivity at a range of 200–600 °C in the presence of excess O₂ (8%) and H₂O (10%).

1. INTRODUCTION

Current technology for diesel exhaust aftertreatment uses selective catalytic reduction (SCR) of NOₓ by NH₃. When excess NH₃ is used to maximize NO conversion, unreacted low-concentration NH₃ (normally <500 ppm) is purified by a downstream catalyst, i.e., an ammonia slip catalyst (ASC), before releasing into the atmosphere. A principal challenge in ASC development is achieving both high activity and selectivity have not yet been developed. A typical example is supported Pt catalysts, such as Pt/Al₂O₃, which exhibit sufficient activities at low temperatures but inevitably produce considerable undesired byproducts of NO, NO₂, and N₂O. To address this problem, a bilayer catalyst configuration comprising catalysts for NH₃ oxidation (Pt) and selective NH₃−SCR (zeolites) was commercialized. These conventional catalysts for low-temperature NH₃ oxidation comprise highly dispersed active nanoparticles supported on porous materials with large specific surface areas. By contrast, we recently reported another possible approach to designing an ASC, where this method uses a nonporous metal thin film prepared via pulsed arc plasma (AP) deposition. We found that the as-prepared nanometer-thick Pt overlayer structure formed on the metal foil substrate exhibited high NH₃ oxidation activity comparable or superior to that of Pt/Al₂O₃. Furthermore, we demonstrated a light-off performance at ≥200 °C using a monolithic honeycomb comprising the metal foils at a gas hourly space velocity (GHSV) of 1.2 × 10⁵ h⁻¹. Despite having fewer active sites than Pt nanoparticles, the extremely high turnover frequency (TOF) of the Pt overlayer enables higher overall reaction rates than the latter, with the high-TOF explained by the increased resistance of the metallic Pt species against oxidation in the presence of excess O₂ relative to the Pt nanoparticles, which are readily oxidized to Pt oxide. Among the undesired byproducts, NO and NO₂ can be converted to N₂ by combining with an NH₃−SCR catalyst in a tandem reactor configuration. However, the Pt overlayer produces a substantial amount of N₂O at relatively low temperatures (200–400 °C). Considering the strong greenhouse effect and the potential for destruction of the stratospheric ozone, the formation of N₂O should be substantially suppressed in practical applications.

Received: November 7, 2020
Accepted: December 2, 2020
Published: December 11, 2020
As an alternative to supported Pt catalysts, supported Ir catalysts are less selective for N₂O and thus more selective for N₂. These studies explained the lower N₂O production on Ir relative to that on Pt by the higher activity of Ir to dissociate NO, which is a byproduct of NH₃ oxidation, with the reduced NO lifetime on the surface negatively affecting N₂O formation. In our previous study, we obtained a preliminary result showing a low light-off temperature of NH₃ oxidation over the Ir overlayer comparable with that over the Pt overlayer. However, the product selectivity and thermal stability of the Ir overlayer have yet to be examined thoroughly under an ASC condition. In the present study, we formed a nanometric Ir overlayer on a SUS foil substrate using the AP technique. Because of its excellent mechanical behavior and resistance to oxidation and corrosion at high temperatures, the metal foil has been widely used as a substrate for an automotive catalytic converter. Catalytic NH₃ oxidation was then conducted under a simulated diesel exhaust condition in the presence of 8% O₂ and 10% H₂O using the as-prepared Ir overlayer (Ir/SUS); the performance of which was compared with that of the Pt overlayer (Pt/SUS) described in our previous study and focusing on differences in product selectivity. We discussed the structure—activity relationship in terms of TOF, oxidation stability, and thermal stability under simulated exhaust gas conditions. We found that the dual-layer deposition of Zr and Ir (Ir/Zr/SUS) was useful for mitigating the thermal deterioration of the thin-film catalyst. Furthermore, we conducted the selective oxidation of NH₃ to N₂ at low temperatures by combining the Ir overlayer catalyst with the V₂O₅/TiO₂-based SCR catalyst in a tandem reactor configuration.

2. RESULTS AND DISCUSSION

2.1. Structure of the Ir Overlayer Catalysts. The X-ray photoelectron spectroscopic (XPS) analysis of the as-prepared Ir/SUS showed strong Ir 4f peaks, whereas peaks due to Fe, Cr, and Al in the SUS foil substrate disappeared (Figure S1 in the Supporting Information), demonstrating that the surface was fully covered by an Ir overlayer. The thickness of the Ir overlayer measured using a quartz crystal microbalance was ≈12 nm at 2000 shots of AP pulses (Supporting Information, Figure S2), with the surface dominantly in the metallic state (Ir⁷⁺). Figure 1 compares the X-ray diffraction (XRD) data of the as-prepared Ir/SUS and a neat SUS foil, Here, the number of AP pulses was increased to 16 000 shots to ensure the reflection intensity. The Ir/SUS showed diffraction peaks assigned to 111, 200, 220, 311, and 222 reflections with a face-centered cubic (fcc) structure. The observed relative intensity ratio of I₁₁₁/I₂₂₀ ≈ 100:7.6:3.5 relative to that of the theoretical intensity ratio (I₁₁₁/I₂₂₀ = 100:48:29), indicating an intense 111 peak. This suggested a strong (111) orientation of the Ir overlayer formed on the SUS foil possibly because the (111) plane offers the lowest surface energy among the various low index faces. Although a similar orientation was reported in Pt/SUS and Rh/SUS samples, this trend did not suggest that the flat (111) plane was exposed on the metal overlayer, as we subsequently revealed a surface roughness for the SUS foil of ≈500 nm. The Ir overlayer structure remained unchanged in the Ir/Zr/SUS sample, where a Zr buffer layer with a thickness of 250 nm was inserted between the Ir overlayer and the SUS foil, as shown in Figure 1b. An additional broad peak appearing between 33 and 35° was due to an amorphous Zr metal phase.

2.2. NH₃ Oxidation Activity of the Ir Overlayer Catalysts. The NH₃ oxidation activity of the as-prepared Ir/SUS was compared with a reference Pt/SUS, which was studied previously. Figure 2 shows the temperature dependencies of the concentrations of NH₃, N₂, N₂O, NO, and NO₂ in the effluent gas from these catalyst beds. Both catalysts initiated N₂H conversion at a low temperature of ~200 °C, which rapidly increased along with an increase in temperature up to 300 °C. However, their product selectivities in this temperature range were quite different. Pt/SUS dominantly yielded N₂O with a high selectivity of ~70% at 225 °C, whereas Ir/SUS exhibited a low selectivity for N₂O (<5%) at the same temperature. The formation of N₂O rapidly decreased at elevated temperatures (>300 °C), at which both catalysts mainly formed NO. Additionally, the temperature dependence of NO₂ formation was similar to that of NO₂, although its selectivity did not exceed 15%. The concentration of formed N₂, which was estimated from the mass balance, was the highest at <300 °C. A higher N₂ selectivity of 75% was observed for Ir/SUS at 225 °C as compared with 22% for Pt/SUS. These marked differences in the product selectivity of NH₃ oxidation were similar to those reported for supported nanoparticle catalysts of Pt and Ir. A higher selectivity for N₂ relative to N₂O is a notably superior characteristic of the Ir overlayer as compared with a Pt overlayer. Besides their different product selectivity, notably, both catalysts showed irregular NH₃ conversion behavior at higher temperatures. The NH₃ conversion over Pt/SUS began to decrease at ≥500 °C because of the structural deterioration of the Pt overlayer. As previously reported, this deterioration was accompanied by a decrease in the Pt surface coverage from 100 to 18%. The Ir/SUS catalyst showed a similar but more extensive deterioration commencing at a temperature as low as 400 °C. Thus, the thermal stability of the Ir overlayer appears to be less than that of the Pt overlayer and requires improvement.

Because Ir/SUS showed high NH₃ oxidation activity but low N₂O selectivity, we compared this remarkable feature with a reference powder catalyst (0.4 wt % Ir/Al₂O₃) to gain insights into the mechanism of the Ir overlayer catalyst compared to...
the Ir nanoparticle catalyst. As shown in Figure 3, the NH₃ oxidation activity of Ir/Al₂O₃ was dependent on pretreatment. The catalyst as-calcined at 600 °C in air showed a low activity, whereas the catalyst after H₂ reduction treatment at 400 °C showed much higher activity. At a temperature range of 200−300 °C, NH₃ conversion and product selectivity over the reduced catalyst were similar to those of Ir/SUS (Figure 2).

Additionally, Ir 4f XPS results suggested that the fractions of metallic Ir (Ir⁰/Ir) in the as-calcined and H₂-reduced Ir/Al₂O₃ were 10 and 100%, respectively (Figure S3). These results suggested that Ir species should be more active in the metallic state rather than in the oxide state. We subsequently used H₂-reduced Ir/Al₂O₃ as a reference catalyst for kinetics analysis.

We revealed that an Ir overlayer has potential advantages over the nanoparticle catalyst (Ir/Al₂O₃). In Table 1, the TOFs for NH₃ conversion over Ir/SUS and Ir/Al₂O₃ at 200 °C are compared (for detailed information on the TOF calculation method, see Table S1 in the Supporting Information).

**Table 1. Activity Comparison between Ir/SUS and Ir/Al₂O₃ for Catalytic NH₃ Oxidation**

| catalyst                  | Ir surface area (m²) | surface Ir (μmol) | NH₃ conv. (%) | reaction rate (μmol min⁻¹) | TOF (min⁻¹) |
|---------------------------|----------------------|-------------------|---------------|---------------------------|-------------|
| Ir/SUS (2000 shots, 90 mm²) | 0.90 × 10⁻⁴         | 0.00234⁵         | 4.7          | 6.29 × 10⁻²             | 26.8       |
| Ir/Al₂O₃ (0.4 wt %, 50 mg)  | 0.795⁶               | 0.0227          | 22.7         | 30.38 × 10⁻²            | 0.38       |

\(^5\) Determined by the geometric area of the foil surface, surface coverage, and surface atomic density of Ir (111) (1.567 × 10¹⁹ atom m⁻²).

\(^6\) Determined by assuming cuboctahedral Ir₅₅ with a ~1 nm quasispherical shape, which has 42 surface Ir atoms (metal dispersion: 0.764). The size was nearly consistent with HAADF-STEM images (Figure S4 and Table S1 in the Supporting Information).

NH₃ conversion at 200 °C. Gas feed: NH₃ (300 ppm), O₂ (8%), H₂O (10%), balanced by He, and 100 mL min⁻¹. TOF: Turnover frequency of NH₃ conversion at 200 °C.

The number of surface Ir sites on Ir/SUS was determined based on the geometric area (3 × 30 mm²) of the Ir coating layer. This method was verified by our previous finding that the true surface area of an SUS foil is almost equivalent to the geometric surface area based on the result of confocal laser scanning microscopy analysis. Because the Ir overlayer exhibited the (111) orientation (Figure 1), the atomic density of the Ir(111) plane was applied. The number of surface Ir sites in the reference catalyst (0.4 wt % Ir/Al₂O₃, 50 mg) was determined by the average Ir particle size (~1 nm) determined by a scanning transmission electron microscope equipped with a high-angle annular dark-field detector (HAADF-STEM, Figure S4 in the Supporting Information). The Ir/Al₂O₃ catalyst contained ~340-fold greater surface Ir sites than those of Ir/SUS. The TOF for the Ir/SUS catalyst based on these data and the NH₃ conversion rate at 200 °C was calculated as 26.8 min⁻¹, which was >70-fold higher compared to that of the Ir/Al₂O₃ catalyst (0.38 min⁻¹). We confirmed
that the size dependence of TOF for Ir nanoparticles was not such large. An Ir/Al₂O₃ catalyst with a larger particle size (5 nm) yielded TOF of 0.88 min⁻¹, only slightly larger than the 1 nm sized catalyst. Therefore, the large difference observed in the TOF between the Ir nanoparticle and the Ir overlayer cannot be explained by a simple size effect. The occurrence of high-TOF NH₃ oxidation plays a key role in enhancing the apparent catalytic activity by the limited number of active sites on the Ir overlayer.

The high-TOF NH₃ oxidation of the present Ir overlayer catalyst resembles that observed for the Pt overlayer in our previous study. The higher TOF for the Pt overlayer (Pt/SUS) relative to that for Pt nanoparticles (Pt/Al₂O₃) can be explained by the different oxidation behavior of Pt: metallic Pt nanoparticles were easily oxidized during the NH₃ oxidation reaction, whereas the metallic Pt overlayer was more stable in Pt/SUS. NH₃ oxidation on Pt proceeds via N–H bond cleavage activated by dissociatively adsorbed O₂ and metallic Pt is a superior catalyst to Pt oxides for the O₂ dissociation. However, the details of the mechanism for the high-TOF NH₃ oxidation over the present Ir overlayer catalyst have remained unknown. To find further information regarding the mechanism, we analyzed the change of the oxidation state of Ir/SUS and Ir/Al₂O₃ by XPS after catalytic NH₃ oxidation at 250 °C for 1 h. As shown in Figure 4, Ir⁰/Ir in the H₂-reduced Ir/Al₂O₃ rapidly decreased from 100 to 48% because of the oxidation to Ir oxides (Ir⁴⁺ and Ir⁵⁺) in the presence of 8% O₂ in the gas phase. Conversely, no obvious change was apparent during the duration for Ir/SUS; the Ir⁰ species in Ir/SUS were stabilized at this reaction temperature. The results of XPS in Figure 4 did not change when the catalytic reaction time at 250 °C was extended by 1 h or more, where the catalytic activity was also stabilized. These results indicate that the extent of Ir oxidation is temperature-dependent under the same reaction atmosphere.

We also analyzed the NH₃ conversion rates over Ir/SUS and Ir/Al₂O₃ catalysts to determine reaction partial orders relative to NH₃, O₂, and H₂O pressures (Figure S5 in the Supporting Information), which is summarized in Table 2. The Ir/Al₂O₃ catalyst showed a positive reaction order in NH₃ (1.10) and negative orders for O₂ (−1.81) and H₂O (−1.01). This suggests that the Ir surface is more inclined to be dominated by adsorbed O₂ and H₂O due to their abundance in the reaction atmosphere. By contrast, the Ir/SUS catalyst exhibited notably different behaviors and provided less negative orders for both O₂ (−0.81) and H₂O (−0.13). The weakly bounded O atoms are a possible explanation for the mitigated O₂ inhibition on Ir/SUS, which is in accordance with the XPS results (Figure 4). Another difference between Ir/SUS and Ir/Al₂O₃ was the orders with respect to H₂O, which might be associated with surface hydrophilicity. The ease of oxidation for Ir/Al₂O₃ is afforded by the hydrophilic surface as compared with the metallic surface of Ir/SUS, thereby making it more susceptible to the complete adsorption of H₂O. These situations might explain the higher TOF for NH₃ oxidation over the Ir overlayer relative to the Ir nanoparticles.

### 2.3. Thermal Stabilization of the Ir Overlayer

As shown in Figure 2, thermal degradation occurred on Ir/SUS at temperatures >400 °C. According to XPS analysis before and after the catalytic activity test up to 600 °C (Figure S6 in the Supporting Information), the surface compositions of Ir/SUS are summarized as shown in Table 3. The Ir surface concentration dropped significantly from 100 to 29%, demonstrating a decrease in Ir surface coverage on the Ir/SUS foil catalyst and exposure of an inactive surface on the SUS substrate. Thus, the Ir overlayer was thermally unstable under the reaction atmosphere at ≥400 °C. Notably, Ir⁰/Ir in the as-prepared Ir/SUS rapidly decreased from 78 to 41% after the use in the catalytic activity test up to 600 °C. This was less pronounced compared to Ir/Al₂O₃, Ir⁰/Ir of which decreased from 100 to 22% (Figure S3 in the Supporting Information). Under the NH₃ oxidation condition at 250 °C, the metallic Ir species in Ir/SUS were stabilized as described above (Figure 4). However, this stabilization effect may not be strong enough to withstand the high-temperature conditions.
Furthermore, accelerated thermal aging of Ir/Zr/SUS at 650 °C suggested that Ir/Zr/SUS preserved an Ir coverage of 94% after the characteristic feature of Ir catalysts. Moreover, Table 3 shows the (111) oriented structure (Figure 1). The NH3 oxidation in the Supporting Information), which was characterized by the Ir overlayer remained unchanged (Table S1 in the Supporting Information). However, unlike Ir/SUS (Figure 2), Ir/Zr/SUS showed no indication of thermal deterioration up to 600 °C. Additionally, the low selectivity for N2O was not affected by the insertion of the Zr buffer layer because it is placed at the most downstream position of the diesel exhaust treatment system, the present result suggests that further improvement is required to suppress the Ir oxidation under the reaction condition. We consider structural and compositional modification of the overlayer to be a significant improvement, which is still under investigation.

Table 3. Surface Compositions of Ir/SUS and Ir/Zr/SUS Determined by XPS

| catalyst† | AP pulse b/shot (Ir) | Ir (%) | Zr (%) | Fe (%) | Cr (%) | Al (%) | Ir0/Ir (%) |
|-----------|----------------------|--------|--------|--------|--------|--------|------------|
| Ir/SUS fresh | 2000 | 100 | 0 | 0 | 0 | 70 | |
| Ir/SUS spent | 2000 | 29 | 58 | 10 | 3 | 41 | |
| Ir/Zr/SUS fresh | 2000 | 100 | 0 | 0 | 0 | 70 | |
| Ir/Zr/SUS spent | 2000 | 94 | 6 | 0 | 0 | 13 | |

“Spent: after the catalytic reaction test up to 600 °C. b The thickness of the Ir overlayer was 12 nm (2000 shots). The thickness of the Zr buffer layer was 250 nm (20 000 shots). “The fraction of metallic Ir determined by Ir 4f XPS.

to suppress the Ir oxidation at high temperatures up to 600 °C. Therefore, the deterioration of Ir/SUS possibly proceeds via the destruction of the Ir overlayer and the oxidation of the Ir surface.

To improve thermal stability, we examined the insertion of a Zr buffer layer between the Ir overlayer and the SUS substrate on the basis of its proven efficiency for Rh/SUS and Pt/SUS overlayer structures.30,40 We then prepared a bilayer structure of Ir/Zr/SUS using a 12 nm thick Ir overlayer and a 250 nm thick Zr buffer layer (Scheme 1). Similar to Ir/SUS, the surface of Ir/Zr/SUS was fully covered by the Ir overlayer (Figure S1 in the Supporting Information), which was characterized by the (111) oriented structure (Figure 1). The NH3 oxidation activity of Ir/Zr/SUS as a function of temperature is shown in Figure S. A rapid light-off of NH3 occurred at ≥200 °C; this suggested that the occurrence of high-TOF NH3 oxidation over the Ir overlayer remained unchanged (Table S1 in the Supporting Information). However, unlike Ir/SUS (Figure 2), Ir/Zr/SUS showed no indication of thermal deterioration up to 600 °C. Additionally, the low selectivity for N2O was not affected by the insertion of the Zr buffer layer because it is a characteristic feature of Ir catalysts. Moreover, Table 3 shows that Ir/Zr/SUS preserved an Ir coverage of 94% after the catalytic test up to 600 °C compared with 29% for the Ir/SUS. Furthermore, accelerated thermal aging of Ir/Zr/SUS at 650 °C for 24 h in a flow of 10% H2O in air preserved the Ir coverage as high as 93% (not shown). These results were according to the thermal stability of the Ir/Zr bilayer structure. Notably, the decrease of Ir0/Ir from 70 to 13% in Ir/Zr/SUS was more than that observed in Ir/SUS (from 78 to 41%). This suggested that compared to Ir/SUS, Ir/Zr/SUS is more susceptible to oxidation at elevated temperatures. As described, metallic Ir is more active than Ir oxides for NH3 oxidation; therefore, the oxidation of Ir is a possible explanation for incomplete NH3 conversion, even at temperatures close to 600 °C (Figure S). One may consider the influence of external mass transfer limitations and/or gas bypass around the thin metal foil strip. However, these influences can be ruled out because the Pt/Zr/SUS sample with the same dimension achieved the almost complete conversion of NH3 above 400 °C.30 Although the temperature of ASC is generally lower than 500 °C because it is placed at the most downstream position of the diesel exhaust treatment system, the present result suggests that further improvement is required to suppress the Ir oxidation under the reaction condition. We consider structural and compositional modification of the overlayer to be a significant improvement, which is still under investigation.

2.4. Tandem Reactor for Selective NH3 Conversion to N2. We revealed that the Ir overlayer achieved efficient NH3 conversion activity at temperatures ≥200 °C, which was comparable with that of Pt/SUS in our previous study.30 The advantage of Ir compared with that of Pt is suppression formation of unfavorable N2O at lower temperatures (200–400 °C, Figure 2). However, the high product selectivity for NO and NO2 rather than N2 at higher temperatures (>300 °C) required improvement. To overcome this shortcoming, two-stage reactions using an NH3 oxidation catalyst and an SCR catalyst offer a promising solution to selective NH3 to N2 conversion.30 In the commercialized dual-layer ASC configuration using a monolithic cordierite honeycomb,28,29 unselective NH3−O2 reaction products (NO and NO2) formed over the Pt/Al2O3 layer can subsequently react selectively with NH3 over the SCR catalyst layer. Instead of the practical catalyst configuration, we used a tandem catalytic reactor system (Figure 6). The simulated gas feed was split into two flow paths. One flow entered the upstream catalyst bed for the NH3−O2 reaction and subsequently transferred to the downstream bed for the NH3−SCR reaction. The other flow was supplied directly to the downstream bed. The overall reaction corresponds to selective NH3 oxidation to N2. We used a V2O5−WO3/TiO2 powder catalyst as a model SCR.
achieved selective NH3 oxidation to N2. Additionally, a feature is in stark contrast to that of Pt/Zr/SUS in a downstream bed according to its allowance of high NO/NO2 conversion at temperatures as low as 350 °C.45

Figure 6 shows the results of the tandem reactors comprising Ir/Zr/SUS in the upstream bed and the downstream SCR bed compared with Ir/Zr/SUS alone. At 350 °C, Ir/Zr/SUS yielded ~194 ppm NO and ~16 ppm NO2 (Figure 6a), which were further lowered to ~0 and ~2 ppm, respectively, in the tandem reactor (Figure 6c). Given that the NH3 conversion was nearly as that by the Ir/Zr/SUS, the SCR catalyst alone was not able to accelerate the NH3→O2 reaction but rather promoted conversion of almost all NO + NO2 to N2 in the downstream bed. Thus, the tandem reactor cooperatively achieved selective NH3 oxidation to N2. Additionally, a comparison of these results with those in a similar tandem reactor comprising Pt/Zr/SUS and the SCR catalyst from our previous report30 is also shown in Figure 6. Unlike the present case, a considerable concentration of N2O formed by Pt/Zr/SUS in a downstream bed. Eflfflffbed. To further enhance the activity, the surface modification of the Ir overlayer is currently under investigation. Additionally, the structure of dual reactors suitable for a practical ASC configuration should be considered. Additionally, the structure of dual reactors suitable for a practical ASC configuration should be considered to avoid the increase of the complexity of the exhaust aftertreatment system.

3. METHODS AND MATERIALS

3.1. Catalyst Preparation and Characterization. Ir overlayer catalysts were formed on an Fe−Cr−Al metal (SUS) foil comprising 75 at% Fe, 20 at% Cr, and 5 atom% Al (50 μm thick, Nippon Steel Chemical and Material, Japan) using pulsed cathodic AP deposition, which was conducted at an ambient temperature, as described in our previous report (Figure S8 in the Supporting Information).30,34–39 The instrumental setup comprised a vacuum chamber connected to a turbo-molecular pump (UTM-50; Ulvac, Japan), an arc discharge source (ARL-300; Ulvac, Japan) fitted with a metal cathode (φ10 mm, 99.9% Furuuya Metals, Japan), and a stage for metal foil substrates. When the pressure reached 10−3 Pa, 2000 shots of AP pulses (2 kA current amplitude and 0.2 ms time period) were made on the Ir metal cathode with a frequency of 1 Hz. The plasma thus generated was irradiated on an SUS foil (30 × 30 mm2) to deposit an Ir metal overlayer on the surface. The thickness of the Ir overlayer during pulsing was monitored using a quartz crystal microbalance (STM-2; Inficon, Switzerland). As illustrated in Scheme 1, the as-prepared metal foil catalysts with one side coated with the Ir overlayer are referred to as Ir/SUS. To improve thermal stability, a bilayer structure with a Zr buffer layer (Ir/Zr/SUS) was also prepared using a sequential step-by-step AP deposition process.40 First, a 250 nm thick Zr buffer layer was formed on the SUS foil (20 000 shots), followed by the formation of a top Ir layer (2000 shots). The Pt overlayer catalysts (Pt/SUS and Pt/Zr/SUS) were also prepared using the same procedure as that for the reference catalysts. A supported Ir nanoparticle catalyst in powder form (0.4 wt % Ir/Al2O3) was prepared by impregnation of aqueous H2IrCl6 (Tanaka Kikinzoku, Japan) onto γ-Al2O3 (JRC-ALO-8; Catalysts Society of Japan; S BET = 150 m2 g−1), followed by calcination at 600 °C for 3 h. The as-obtained catalyst was then treated under a stream of 20% H2/N2 at 400 °C for 3 h to deposit the Ir metal nanoparticles.

The crystal structure of the as-prepared overlayer catalysts was determined using XRD obtained from the application of monochromatic Cu Kα radiation at 40 kV and 200 mA (RINT-TTR III; Rigaku, Japan) in a symmetric 2θ−θ scan mode. Surface analysis was conducted using a K-alpha X-ray photoelectron spectrophotometer (Thermo Fisher Scientific) with monochromatic Al Kα radiation. A charge correction was made using the C 1s binding energy at 285 eV. A 200 kV FEI TECNAI F20 scanning transmission electron microscope (STEM) equipped with a high-angle annular dark-field detector (HAADF) was used to determine the Ir metal particle size (200 kV).

3.2. Catalytic Reactions. A strip foil (3 × 30 mm2, as shown in Scheme 1) with one side coated with the Ir overlayer was used for catalytic tests, which were performed in a flow reactor in a steady-state mode (Figure S9 in the Supporting Information). The catalyst was fixed in a quartz tube with an inner diameter of 4 mm. To simulate a condition of diesel exhaust, a gas mixture containing 300 ppm NH3, 8% O2, 10%...
H2O, and a He balance was supplied at 100 mL min⁻¹. The gas flow rate corresponds to a GHSV of ∼60 000 h⁻¹ when a reference powder catalyst (0.4 wt % Ir/Al2O3, 50 mg, 20 mesh) was used. A Fourier-transform infrared spectrometer ( Nicolet iS50; Thermo Fisher Scientific) with a 2 m gas cell (MARSTM; S. T, Japan) was used to determine the gas concentrations of NH3, NO, N2O, and NO2. The reaction rate dependence on partial pressures of NH3, O2, and H2O was measured under differential conditions at 185 or 195 °C, where the NH3 conversion was almost less than 20%. The NH3 partial pressure in the gas feed varied from 0.005 to 0.04 kPa, with the O2 and H2O partial pressures kept at 8 and 10 kPa, respectively. When the NH3 partial pressure was kept at 0.03 kPa, the O2 and H2O partial pressures varied from 0.5 to 10 kPa. The total gas flow rate was kept constant at 100 mL min⁻¹ (He balance).

A tandem reactor comprising of an overlayer catalyst and an NH3−SCR catalyst was also evaluated. As a model SCR catalyst, V2O5−WO3/TiO2 with the composition of 1 wt % V2O5, 10 wt % WO3, and 89 wt % TiO2 was prepared by wet impregnation. Aqueous solutions of ammonium metavanadate (NH4VO3) and ammonium metatungstate ([NH4]6W7O24; Wako Pure Chemical, Japan) were impregnated onto TiO2 (anatase, JRC-T10-14; supplied by Catalysis Society of Japan) and subsequently dried and calcined at 550 °C for 3 h. In the tandem reactor experiment, a gas mixture (300 ppm NH3, 8% O2, 10% H2O, and a He balance of 50 mL min⁻¹) was supplied to the Ir/Zr/SUS catalyst (a 3 × 30 mm² strip with one side coated) in an upstream bed. The effluent gas was then supplied together with another gas feed (300 ppm NH3, 8% O2, 10% H2O, and a He balance of 50 mL min⁻¹) to the V2O5−WO3/TiO2 catalyst (100 mg, 20 mesh) in a downstream bed. The reference Pt/Zr/SUS catalyst was also used in an upstream bed.

4. CONCLUSIONS
In summary, an Ir overlayer formed onto a metal foil substrate via pulsed AP deposition and demonstrated high NH3 oxidation activity in the presence of excess O2 (8%) and H2O (10%). At 225 °C, the Ir overlayer catalyst exhibited a much lower selectivity for undesirable N2O (<5%) compared with that of the Pt overlayer catalyst (~70%). Other undesired byproducts (NO and NO2) were able to be converted efficiently to N2 using a tandem reactor that comprises the Ir overlayer catalyst and an SCR catalyst (V2O5−WO3/TiO2) placed in upstream and downstream beds, respectively. The high NH3 oxidation rate was confirmed by a >70-fold higher TOF relative to that of the Ir nanoparticles in the Ir/Al2O3 powder catalyst. Despite the small number of active sites in the Ir overlayer structure, the higher TOF enabled superior overall reaction rates. Moreover, the high TOF was associated with the higher stability of metallic Ir against oxidation relative to less active Ir oxides in an Ir overlayer compared with that in Ir nanoparticles. Furthermore, inserting a 250 nm thick Zr buffer layer between the Ir overlayer and the metal foil substrate successfully enhanced the thermal stability required for practical applications. These findings demonstrated the Ir overlayer structure as a promising environmentally benign ASC for diesel exhaust purification applications.

ASSOCIATED CONTENT
1 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05443.

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The manuscript was written with contributions from all named authors. Each author has approved the final version of the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was supported by the Ministry of Education Culture, Sports, Science and Technology (MEXT) program,
Elements Strategy Initiative to Form Core Research Center (JPMXP0112101003)

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