



Development of the Chemical Reaction Mechanism for Oxide Film Formation and Decomposition in Rh-Based Three-Way Catalysts

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Abstract

A full-hybrid system incorporating a spark-ignition engine is regarded as essential for future passenger car powertrains. To achieve effective exhaust-gas purification in such vehicles, it is necessary to elucidate the characteristics of three-way catalysts and to develop both phenomenon-based models and numerical prediction techniques. Previous studies examined the influence of surface oxidation—caused by exposure to oxygen-rich conditions during fuel cut-off in deceleration and engine stop in HEVs—on the purification performance of Rh, one of the most active precious metals used in three-way catalysts. CO–O₂ light-off tests showed that the light-off curve shifted to higher temperatures after lean pretreatment compared with rich pretreatment. XPS analysis further indicated the formation of a reversible oxide film under lean conditions. In this study, the CO–NO light-off test was conducted three times following lean-atmosphere pretreatment. The second and third light-off curves rose markedly faster than the first, yet did not coincide with the curve obtained after hydrogen reduction. Moreover, the second and third curves were nearly identical, suggesting that only part of the oxide film formed under lean conditions may have been decomposed during the CO–NO light-off process. Previous work has also emphasized the importance of maintaining thermodynamic consistency when modeling chemical reactions occurring on catalyst surfaces. By incorporating NO-related surface reactions into the previously developed model and revising parts of the reaction scheme to ensure thermodynamic consistency, the simulation was able to reproduce the formation and decomposition behavior of oxide films and their influence on CO–NO purification performance.

Keywords Strong hybrid system · Three-way catalyst · Rh · Oxide film · CO–NO · Numerical simulation

1 Introduction

In recent years, automotive emission regulations have become increasingly stringent. Euro 7, scheduled for implementation in January 2028 for passenger cars and vans, will impose stricter limits on NO_x and other pollutants, making it one of the most rigorous standards globally [1]. Although

the EU market currently offers 370 BEV models, including 16 priced below €30,000, demand remains limited. BEV market share in 2024 was below 14% and demand has remained stable, with no sign of the anticipated “hockey-stick” growth curve over the past few years. In fact, BEV market share has largely stagnated and has fallen far short of the previously forecasted 25–30% [2]. Considering these circumstances, the EU announced in December 2025 a revision of its plan to ban sales of new gasoline and diesel vehicles by 2035. Under the revised plan [3], CO₂ will be reduced by 90% by 2035 compared to 2021. Therefore, HEVs and PHEVs, which have high energy conversion efficiency and use carbon-neutral fuels such as e-fuels, biofuels, and hydrogen, are promising technologies. Consequently, the use of three-way catalysts, which play a critical role in reducing emissions from spark ignition engines, will remain essential in the future. A three-way catalyst is a device that converts the three harmful components found in the exhaust gas of spark-ignition engines—CO, HC and NO_x—into

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harmless substances such as N_2 , H_2O and CO_2 . The active metals used in three-way catalysts include Pt, Pd and Rh [4].

When comparing the properties of precious metals, Rh demonstrates superior stability in maintaining small particle size even after extended exposure to high temperatures, resulting in a greater number of active sites compared to Pt and Pd. This characteristic is considered the primary reason for Rh's outstanding exhaust gas purification performance. Furthermore, Iwachido et al. compared the emission performance of Rh, Pt, and Pd catalysts at an equal loading of 2.0 g/L [5], showing that Rh provides significantly better NO_x purification than Pt and Pd at the same level. In the mechanism of NO_x purification, the crucial step is the cleavage of the N–O bond in adsorbed NO, and one possible reason for the excellent NO_x purification performance of Rh is its ability to readily break this N–O bond [6]. Based on these observations, this study focuses on Rh catalysts, which maintain high performance even after thermal aging and are most suitable for NO_x removal.

The surface condition of precious metals determines the catalyst's purification performance. It is reported that this surface state can vary depending on the operating conditions of spark-ignition engines. When power demand rises during sudden acceleration or towing on a long incline, the mixture becomes richer due to fuel enrichment and the cooling effect of fuel evaporation under high-load conditions. This reduces the charge temperature, causing the excess air ratio in spark-ignition engines to shift to rich, which leads to HC poisoning [7] on the metal surface. Conversely, when the engine shuts down in a strong hybrid system, fuel supply is cut off during deceleration, or λ -switching becomes unstable, air rushes in and the excess air ratio becomes lean, forming an oxide film on the metal surface. These phenomena degrade purification performance. Therefore, it is essential to clarify the mechanisms behind these changes and develop countermeasures that enable rapid recovery to maintain high catalytic efficiency.

It has been confirmed that Pd and Rh purification performance varies depending on the oxidation state of the metal surface. Gustafson et al. [8] concluded that the oxidation states of Pd can be categorized into three stages: the surface oxide, the thin epitaxial bulk oxide, and the bulk oxide grown sufficiently thick. In the first two stages, the PdO surface exposing coordinatively unsaturated Pd atoms serves as active sites. However, when a sufficiently thick bulk oxide forms, the surface exposes a more stable plane without such unsaturated Pd atoms, resulting in loss of activity. Thus, it has been clarified that Pd retains catalytic activity comparable to its metallic state under oxidizing conditions, as long as a thick oxide film does not develop on the surface. There are also reports indicating that, with respect to the oxidation state of Pd, the highest catalytic purification performance is

achieved when Pd and PdO coexist as a mixed phase [9]. On the other hand, metallic Rh exhibits higher catalytic activity than oxidized Rh. Minokoshi et al. [10] investigated how different Rh surface states affect light-off performance. The influence of pretreatment conditions on the fraction of metallic Rh and the resulting light-off behavior can be elucidated by comparing two catalyst preparation protocols. Catalysts pretreated under rich conditions consistently exhibited a higher fraction of metallic Rh relative to those pretreated in air. This increased metallic Rh fraction correlated strongly with enhanced CO light-off performance. At all temperatures employed in the CO oxidation tests, samples subjected to rich pretreatment demonstrated both greater metallic Rh coverage and superior purification efficiency. These results collectively indicate that high-temperature exposure to air diminishes the metallic Rh fraction, presumably through oxidation or related deactivation pathways, thereby leading to a deterioration in CO purification performance.

We previously investigated the effect of catalyst pretreatment conditions on the CO–O₂ light-off performance of a Rh/Al₂O₃ catalyst without oxygen storage functionality [11]. XPS analysis revealed that the Rh surface remained partially oxidized even after rich pretreatment, while lean pretreatment further increased the oxide fraction and decreased the metallic Rh fraction. These results suggest the presence of both irreversible oxide, which remains even under rich conditions, and reversible oxide, which forms and decomposes depending on the atmosphere. CO–O₂ light-off tests further showed that lean pretreatment increased T_{50} by approximately 10°C compared with rich pretreatment, indicating that an increase in Rh oxide and a corresponding decrease in metallic Rh sites deteriorate purification performance.

Shimokuri et al. [12] also investigated purification performance in the CO/O₂ system and successfully developed a mechanism capable of reproducing their experimental results. However, their mechanism does not account for the influence of oxide film formation. In the present study, two hypotheses regarding the Rh surface state and its effect on purification performance were formulated based on the experimental findings. To evaluate these hypotheses, numerical simulations were performed using a phenomenological model that describes oxide film formation and decomposition, incorporated into the reaction scheme of a previously published Rh surface mechanism [13], as follows:

The oxide film formation reaction:	$O(s) + O(s) + O(s) \rightarrow O_3(s) + Rh(s)$
The oxide film decomposition reaction:	$O_3(s) + Rh(s) \rightarrow O(s) + O(s) + O(s)$

The first hypothesis posits that trivalent Rh (Rh₂O₃) forms as an oxide film via the intermediate divalent Rh (RhO), reducing the number of active sites and thereby

deteriorating light-off characteristics. The second hypothesis assumes that under relatively high-temperature lean conditions, the conversion from RhO to Rh₂O₃ is approximately 9%, based on XPS results. Under rich conditions at the same temperature, Rh₂O₃ converts back to RhO, resulting in final surface compositions of 20% RhO and 28% Rh₂O₃, also supported by XPS data. Simulation results successfully reproduced the experimental observations from XPS and light-off tests [14].

In addition to the CO–O₂ system, the Rh surface oxidation state also affects the purification of gas mixtures containing CO, NO, C₃H₆, and C₃H₈. Li et al. [15] performed light-off tests using Rh/Al₂O₃ catalysts and found that oxidation at 950°C increased the T₅₀ of all species by approximately 60°C compared with the fresh catalyst. Subsequent reduction substantially restored the purification performance, and higher reduction temperatures resulted in performance nearly equivalent to that of the fresh catalyst. XRD analysis revealed that metallic Rh was converted to Rh₂O₃ after oxidation at 950°C. While Rh₂O₃ remained after reduction at 600°C, it was restored to metallic Rh at 800°C. These results indicate that high-temperature oxidation converts metallic Rh sites to Rh oxide, causing performance deterioration, whereas high-temperature reduction restores metallic Rh sites and catalytic activity.

As the next step, NO will be added to the feed gas, and experimental and numerical analyses will be conducted using a CO–NO system. The model will be improved by modifying part of the reaction scheme based on chemical reactions that can realistically occur on the catalyst surface while maintaining thermodynamic consistency. The following reference was consulted to ensure thermodynamic consistency. Using this model, this study aims to clarify the effect of NO on the formation and decomposition of surface oxides, including Rh₂O₃, which were not considered in previous studies.

Tischer et al. [16] developed the approach that makes it possible to maintain thermodynamic consistency in the reaction mechanism with minimum changes to any reaction rate constant and specify thermodynamic properties of the surface species in the model. Delgado et al. [17] developed a model for methane oxidation on Ni, and Stotz et al. [18] constructed a model for methane oxidation on Pd using a parameter-fitting approach to reproduce experimental results, similar to the previous studies conducted by the authors. When determining the rate constant for each scheme in the model, they also adjusted the parameters so that the overall mechanism satisfies thermodynamic consistency by using the above approach. A reaction mechanism is said to satisfy thermodynamic consistency when the forward and reverse rate constants of every

elementary reaction are defined in accordance with thermodynamic principles. Specifically, the reaction mechanism is thermodynamically consistent if the following equation holds for all elementary reactions. Details will be explained in the numerical simulation section later.

$$\frac{k_{fi}(T)}{k_{ri}(T)} = \frac{K_{ci}(T)}{K_{pi}(T)} \cdot \exp\left(-\frac{\Delta_R G_i(T)}{RT}\right)$$

2 Experimental Methods

2.1 Catalyst Specifications

The catalyst examined in this study is a fresh Al₂O₃-based material, selected to simplify the oxygen transport pathway to the Rh surface exclusively from the gas phase. Detailed catalyst specifications are provided in Table 1. For active site density, both the value for the unused catalyst and the value estimated by the CO adsorption method [21] from a previous report for the used catalyst are listed. In the model calculations discussed later, the value obtained via the CO adsorption method is applied.

2.2 Synthetic Gas Test Bench

Figure 1 shows an overview of the entire setup. High-pressure gas cylinders supply oxygen (O₂), carbon dioxide (CO₂), carbon monoxide (CO), nitrogen oxide (NO), propylene (C₃H₆), and nitrogen (N₂) produced by a nitrogen generator to the cylindrical reactor of the Synthetic Gas Test Bench (SGB). The synthetic gas composition and flow rate are regulated by mass flow controllers, which are operated via a personal computer,

Table 1 Specification of Rh test-piece catalyst

φ×L mm	φ20×50
PGM	Rh
PGM loading g/(L-cat)	0.8
Support material of Al	3% La-Al ₂ O ₃ :γ
Binder	Al ₂ O ₃
Substrate	Cordierite
Cell density cpsi	600
Wall thickness mil	4.3
Cell geometry	Square
Layering	Mono layer
Washcoat g/L	100+Binder 10
Active site density of Al ₂ O ₃ (Fresh, Unused) mol/(m ² -cat)	1.647
Active site density of Al ₂ O ₃ (Fresh, Used) mol/(m ² -cat)	0.8827

in H_2 flow were conducted. After the pretreatment, a light-off test was performed by flowing CO and NO under stoichiometric conditions. In order to determine whether the oxide film presumed to have formed during lean pretreatment remains intact or decomposes after the first light-off

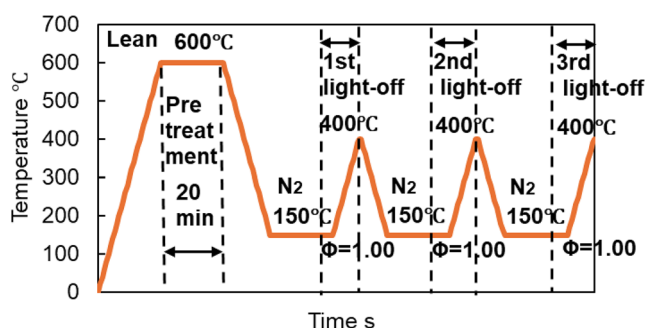


Fig. 2 The light-off experiment program repeated three times after lean pretreatment

Table 2 Gas composition of pretreatments and light-off test

Species	Pretreatments		Light-off
	Lean	H_2 reduction	
O_2 ppm	3500	0	0
NO ppm	0	0	5000
CO ppm	6500	0	5000
H_2 ppm	0	7500	0
N_2 %	Balance gas		
Equivalence ratio (Excess air ratio)	0.9630 (1.038)	0	1.000(1.000)
Space velocity 1/h	50,000		
Temperature °C	600	400	150 to 400 (5 K/min)

performance, the light-off test was repeated three times. The test program is shown in Fig. 2. The test conditions of pretreatments and light-off were listed in Table 2. First, the temperature was raised to 600°C, and CO and O_2 were flowed with a composition that resulted in lean equivalence ratio to perform the pretreatment. Then, under an inert atmosphere of 100% N_2 , the temperature was lowered once and subsequently raised from 150°C to 400°C at a rate of 5 K/min, which was repeated three times. During this process, a mixed gas containing 5000 ppm of CO and 5000 ppm of NO was introduced into the reactor, and the concentrations of CO, NO and CO_2 at each temperature were measured. Additionally, to compare surface conditions based on changes in the light-off curves, a light-off test was also conducted using a catalyst whose surface was fully reduced to the metallic state via hydrogen reduction, under the same gas composition.

Figure 3 shows the results of the repeated light-off tests after lean pretreatment, as well as the results of the light-off test conducted after the oxide film was removed by hydrogen reduction. The figure shows that T_{50} of CO is almost the same as NO. Compared to the first light-off curve, the second light-off curve showed a much faster rise under lower temperatures but never matched the curve obtained after hydrogen reduction. The third light-off curve was roughly consistent with the second, and the performance never recovered to the level observed after hydrogen reduction. When comparing the light-off temperatures at which the conversion rate reached 50%, the values were approximately 260°C after hydrogen reduction, about 280°C after the first test following lean pretreatment, and around 270°C for both the second and

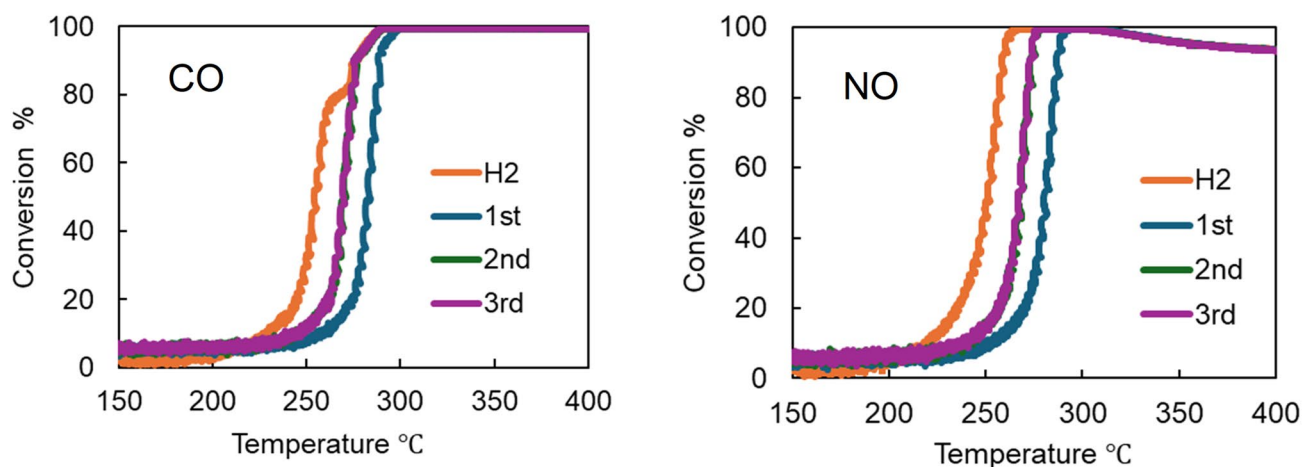


Fig. 3 The comparisons of light-off curves for the 1st, 2nd and 3rd experiments after lean pretreatment and 1st light-off curve after H_2 pretreatment

third tests. These results indicate that although the oxide film formed under lean conditions is partially decomposed during light-off tests, it is not completely removed and only its proportion decreases.

4 Numerical Simulation Results and Discussion

Numerical analysis was conducted using the DETCHEM-CHANNEL model, a chemical simulation software developed by Deutschmann et al. [19]. This chapter mainly describes

the model overview, the chemical reaction schemes considered, the simulation conditions, and the parameters that were adjusted.

4.1 Overviews of the Numerical Model

The DETCHEM^{CHANNEL} model simulates the steady state chemically reacting gas flow through a cylindrical channel using the boundary layer approximation. The governing equations for r-z cylindrical coordinate are given as follows.

$$\text{The total continuity} \quad : \quad \frac{\partial (rpu)}{\partial z} + \frac{\partial (rpv)}{\partial r} = 0 \quad (4.1)$$

$$\text{Axial momentum} \quad : \quad \frac{\partial (rpu^2)}{\partial z} + \frac{\partial (rpuv)}{\partial r} = -r \frac{\partial p}{\partial z} + \frac{\partial}{\partial r} \left(\mu r \frac{\partial u}{\partial r} \right) \quad (4.2)$$

$$\text{Radial momentum} \quad : \quad \frac{\partial p}{\partial r} = 0 \quad (4.3)$$

$$\text{The energy continuity} \quad : \quad \frac{\partial (rpuh)}{\partial z} + \frac{\partial (rpvh)}{\partial r} = u \frac{\partial p}{\partial z} + \frac{\partial}{\partial r} \left(\lambda r \frac{\partial T}{\partial r} \right) - \frac{\partial}{\partial r} \left(\sum s r j_s h_s \right) \quad (4.4)$$

$$\text{The species continuity} \quad : \quad \frac{\partial (rpuY_s)}{\partial z} + \frac{\partial (rpvY_s)}{\partial r} = - \frac{\partial}{\partial r} (r j_s) + r \omega_s \quad (4.5)$$

$$\begin{aligned} \text{The flux} \quad (r < r_{max}) \quad & j_s = -\rho D_s \frac{M_s}{M} \frac{\partial X_s}{\partial r} \\ & (r = r_{max}) \quad j_s = -\dot{r}_s \end{aligned}$$

z	:	Axial coordinate
r	:	Radial coordinate
u	:	Axial component of gas velocity
v	:	Radial component of gas velocity
p	:	Pressure
h	:	Mean specific enthalpy
Y_s	:	Mass fraction of species
X_s	:	Mole fraction of species
μ	:	Viscosity
λ	:	Thermal conductivity
h_s	:	Surface species specific enthalpy
ω_s	:	Gas phase reaction rate
j_s	:	The radial diffusion flux
M_s	:	Species molecular weight
$\bar{M}$	:	Mean molecular weight

4.2 The Reaction Rate Parameters

Typically, the i -th reaction in a reaction mechanism is represented using the stoichiometric coefficients of the

reactants ν'_{ki} , the stoichiometric coefficients of the products ν''_{ki} , and the chemical species X_k , as shown in Eq. (4.7). In the simulation performed with the model developed in this study, the rate constants for each reaction step are defined separately for the forward and reverse directions. Both sets of rate constants are assumed to follow the Arrhenius equation. These Arrhenius expressions are modified to incorporate the effect of surface species coverage, and the adjusted form shown in Eq. (4.8) is used to calculate the rate constants. Subsequently, the i -th reaction rate for each step is determined from the forward and reverse rate constants using Eq. (4.9). Based on this, the production rate of species k is expressed as shown in Eq. (4.10). Additionally, adsorption reactions are treated using Eq. (4.11).

$$\sum_{k=1}^K \nu'_{ki} X_k \quad \frac{k_{fi}}{k_{ri}} \quad \sum_{k=1}^K \nu''_{ki} X_k \quad (4.7)$$

$$k_i = A_i T^{\beta_i} \exp \left(\frac{-E_i}{RT} \right) \prod_{k=K_s^f(N_s^f)}^{K_s^i(N_s^i)} [Z_k(n)]^{\mu_{ki}} \exp \left(\frac{\epsilon_{ki} [Z_k(n)]}{RT} \right) \quad (4.8)$$

$$q_i = k_{fi} \prod_{k=1}^K [X_k]^{\nu'_{ki}} - k_{ri} \prod_{k=1}^K [X_k]^{\nu''_{ki}} \quad (4.9)$$

$$\frac{d[X_k]}{dt} = \sum_{i=1}^I (\nu''_{ki} - \nu'_{ki}) q_i \quad (4.10)$$

$$\frac{d[X_k]}{dt} = S_k^0 \sqrt{\frac{RT}{2\pi M_k}} [X_k] \prod_{k=K_s^f(N_s^f)}^{K_s^i(N_s^i)} [Z_k(n)]^{\mu_{ki} + \nu'_{ki}} \quad (4.11)$$

I	The total number of elementary reactions in the reaction mechanism
K	The total number of chemical species in the reaction mechanism
X_k	Chemical species formula
k_{fi}	Forward rate constants of the i -th reaction
k_{ri}	Reverse rate constants of the i -th reaction
A_i	Pre-exponential factor of the i -th reaction
β_i	Temperature exponent of the i -th reaction
E_i	Activation energy of the i -th reaction
μ_{ki}	Coverage parameters of species k in the i -th reaction
ϵ_{ki}	Coverage parameters of species k in the i -th reaction
q_i	Reaction rate of the i -th reaction
ν'_{ki}	Stoichiometric coefficients on the reaction side in the i -th reaction
ν''_{ki}	Stoichiometric coefficients on the production side in the i -th reaction
S_k^0	Sticking coefficients
$Z_k(\bar{n})$	Surface coverage of species k on the site n

Equation (4.8) introduces two correction terms to the standard Arrhenius expression, each associated with a temperature exponent and activation energy. These terms are influenced by surface coverage, which reflects the occupancy of active sites. To reproduce experimental observations in the simulation, five parameters in Eq. (4.8) were tuned to determine the reaction rate constants for each reaction step.

4.3 Calculation Condition

In a previous study, the adsorption/desorption reactions and surface reactions parameters of the CO oxidation model on Rh surfaces [14] were adjusted based on experimental results using Rh/Al₂O₃ catalysts, thereby constructing a Rh/Al₂O₃ model. This model reasonably reproduced the results of light-off tests for CO+O₂ system and surface state analyses conducted using XPS (X-ray Photoelectron Spectroscopy). In this study, by incorporating reaction schemes involving NO into the model and revising certain existing schemes, we successfully reproduced the light-off test results for CO and NO as target gas species while ensuring thermodynamic consistency. The reaction schemes considered and initial conditions for the simulation are presented below.

4.3.1 Surface Reaction Mechanism

Table 3 summarizes the surface reaction mechanisms employed in this study. Reactions shown in bold were newly developed by the authors, while the remaining reactions are

based on the previous mechanisms [13, 20]. Reactions No. 14 and 15 were added because the original model considered only the reverse direction, which contradicts the principle of thermodynamic consistency. Reactions No. 17 to No. 22 are associated with oxide film formation and decomposition. In previous studies, these processes were represented by the following reactions:

The oxide film formation reaction:	$O(s) + O(s) + O(s) \rightarrow O_3(s) + Rh(s)$
The oxide film decomposition reaction:	$O_3(s) + Rh(s) \rightarrow O(s) + O(s) + O(s)$

However, these schemes involve the simultaneous interaction of three surface species, which is physically unlikely unless extremely high activation energies are assumed. Therefore, in this work, the oxide film formation and decomposition mechanisms were reformulated to occur in two steps, as shown in Table 3. For Reactions No. 21 and 22, the decomposition of the oxide film observed during the light-off test is represented under the assumption that N(s) is involved in the decomposition process.

Among the reactions listed in Table 3, the fitting parameters are shown in bold. First, the parameters for reactions No. 14, 15, and 17–22 were fully determined in this study. Because reaction No. 15 is less likely to occur, its rate constant is set smaller than those of the other reactions. For reaction No. 20, two coverage-dependent coefficients for O₃(s) were introduced so that the decomposition of O₃(s) depends on its initial coverage. In addition, the order of the pre-exponential factors for Reactions No. 9–13 has been set higher than in the original mechanism, because the calculations were performed with a flow rate approximately twice that used in the original mechanism's conditions. Furthermore, for reactions No. 11, 13, and 16, the temperature exponent and activation energy were increased to shift the CO and NO conversion reactions toward higher temperatures.

4.3.2 Initial Conditions

The simulation conditions in the model include the radius of a single cell and the active site density of the catalyst used in the light-off test, the velocity during the light-off test, the measured inlet gas temperature, and the inlet gas composition. In the light-off test simulation, the outlet gas composition of the catalyst was examined, and fitting reaction rate parameters was performed to reproduce the light-off curve shown in Fig. 3. The conditions used in the simulation are listed in Table 4. The velocity values listed in Table 4 correspond to those at 25 °C and 1 atm, and they are varied as the temperature increases.

Table 3 Reaction schemes and parameters used in this work

No	Reaction Scheme	A/S^0	β	E	ε/μ
1	$O_2 + Rh(s) + Rh(s) \rightarrow O(s) + O(s)$	$*1.000 \times 10^{-2}$	0.000	0.000	-
2	$O(s) + O(s) \rightarrow Rh(s) + Rh(s) + O_2$	5.329×10^{22}	-0.137	188.0	-
3	$CO + Rh(s) \rightarrow CO(s)$	$*5.000 \times 10^{-1}$	0.000	0.000	-
4	$CO(s) \rightarrow Rh(s) + CO$	1.300×10^{14}	0.295	134.0	εCO 47.00
5	$CO_2 + Rh(s) \rightarrow CO_2(s)$	$*4.800 \times 10^{-2}$	0.000	0.000	-
6	$CO_2(s) \rightarrow Rh(s) + CO_2$	3.920×10^{11}	0.315	20.51	-
7	$NO + Rh(s) \rightarrow NO(s)$	$*5.000 \times 10^{-1}$	0.000	0.000	-
8	$NO(s) \rightarrow NO + Rh(s)$	2.000×10^{14}	0.000	108.9	-
9	$O(s) + C(s) \rightarrow CO(s) + Rh(s)$	4.629×10^{23}	0.000	92.14	-
10	$CO(s) + Rh(s) \rightarrow O(s) + C(s)$	2.556×10^{23}	-0.000	174.8	εCO 47.00
11	$O(s) + CO(s) \rightarrow CO_2(s) + Rh(s)$	2.073×10^{25}	0.044	165.0	εCO 47.00
12	$CO_2(s) + Rh(s) \rightarrow O(s) + CO(s)$	1.231×10^{25}	-0.110	241.0	-
13	$NO(s) + Rh(s) \rightarrow N(s) + O(s)$	8.800×10^{23}	0.000	136.5	-
14	$N(s) + O(s) \rightarrow NO(s) + Rh(s)$	6.784×10^{23}	-0.046	234.7	εN 8.350
15	$N_2 + Rh(s) + Rh(s) \rightarrow N(s) + N(s)$	7.027×10^{15}	0.500	106.3	-
16	$N(s) + N(s) \rightarrow N_2 + Rh(s) + Rh(s)$	1.204×10^{22}	0.000	151.9	εN 16.70
17	$O(s) + O(s) \rightarrow O_2(s) + Rh(s)$	9.974×10^{21}	-0.427	257.8	-
18	$O_2(s) + Rh(s) \rightarrow O(s) + O(s)$	7.500×10^{23}	-0.000	164.8	-
19	$O_2(s) + O(s) \rightarrow O_3(s)$	6.883×10^{21}	0.000	163.0	-
20	$O_3(s) \rightarrow O_2(s) + O(s)$	1.468×10^{12}	0.000	190.5	εO_3 7.000 μO_3 0.7.00
21	$N(s) + O_2(s) \rightarrow NO(s) + O(s)$	6.280×10^{21}	-0.020	213.0	εN 8.350
22	$NO(s) + O(s) \rightarrow N(s) + O_2(s)$	1.093×10^{22}	-0.400	207.8	-

*Since reactions No. 1, 3, 5, and 7 are adsorption reactions, Eq. (4.11) is used instead of Eq. (4.10)

Table 4 The calculation setting conditions

Temperature K	423.15~673.15
Pressure atm	1.0
The radius of a single cell m	4.979×10^{-4}
Active site density mol/cm ²	3.034×10^{-8}
Velocity m/s	9.500×10^{-1}

4.4 The Result of Mechanism Adjustment

As mentioned in the introduction section, this study aims to develop a model in which the overall mechanism maintains thermodynamic consistency, and the following approach was employed [16].

The following equation relates reaction rates to thermodynamic properties.

$$\frac{k_{fi}(T)}{k_{ri}(T)} = \frac{K_{ci}(T)}{K_{pi}(T)} \cdot \exp\left(-\frac{\Delta_R G_i(T)}{RT}\right)$$

Where $K_{ci}(T)$ and $K_{pi}(T)$ are concentration and pressure equilibrium constants at temperature T in the i -th reaction,

respectively. $\Delta_R G_i(T)$ represents the difference of standard Gibbs energy between the sum of reactants and products at T of the i -th reaction considered. R is the universal gas constant. If this equation holds for all reactions, the constructed reaction mechanism can be considered thermodynamically consistent. Therefore, while it is possible to ensure thermodynamic consistency by manually determining only the forward rate constants and calculating the reverse rate constants from this equation, in constructing a surface reaction mechanism, the thermodynamic properties of surface species are generally unknown. As a result, both forward and reverse rate constants must be specified individually. Consequently, unless Gibbs energies that satisfy this equation are identified, thermodynamic consistency cannot be achieved. To address this, the mechanism is finalized to satisfy thermodynamic consistency using DETCHEM-ADJUST, through the following approach [19].

The equation obtained by taking the logarithm of both sides of the above formula is shown below.

$$\ln k_{fi} - \ln k_{ri} = \ln \frac{K_{ci}(T)}{K_{pi}(T)} - \sum_k v_{ki} \frac{G_{ki}(T)}{RT}$$

Here, it is noted that $v_{ki} = \nu'_{ki} - \nu'_{ki}$. By separating the unknown and known terms and rewriting it to express the necessary adjustment of the rate constants as $x_i(T)$, we obtain the following equation.

$$\ln \frac{K_{ci}(T)}{K_{pi}(T)} - \sum_{\text{known } k} v_{ki} \frac{G_{ki}(T)}{RT} - \sum_{\text{unknown } k} v_{ki} \cdot y_{ki}(T) =$$

Here, $y(T)$ represents the unknown chemical species $\frac{G_{ki}(T)}{RT}$. Using the abbreviation

$$z_i(T) = \ln \frac{K_{ci}(T)}{K_{pi}(T)} - \sum_{\text{known } k} v_{ki} \frac{G_{ki}(T)}{RT} - \ln k_{fi} + \ln k_{ri}$$

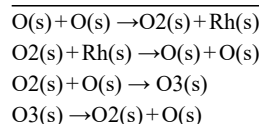
we need to solve a system of linear equations

$$x_{fi}(T) - x_{ri}(T) = z_i(T) - \sum_{\text{unknown } k} v_{ki} \cdot y_{ki}(T)$$

to ensure thermodynamic consistency. Note that the x_{fi} , x_{ri} , y_{ki} and z_i are all functions of temperature of the form $f(T) = a + b \ln T + c/T$ with three parameters a , b and c .

It is not necessary to adjust all reaction schemes using DETCHEM^{ADJUST}. If the mechanism consists of K pairs of reversible reactions with N surface species having unknown thermodynamic parameters, at least $K - N + 1$ reactions must be adjusted.

In this case, $K=11$ and $N=9$, so at least three reactions need to be adjusted.



A summary of the parameters after modifying these two schemes is provided in Table 5 below.

Table 5 Reaction Parameters after adjusting thermodynamic consistency

No	Reaction Scheme	A/S^0	β	E	ϵ/μ
1	$\text{O}_2 + \text{Rh(s)} + \text{Rh(s)} \rightarrow \text{O(s)} + \text{O(s)}$	$*1.000 \times 10^{-2}$	0.000	0.000	-
2	$\text{O(s)} + \text{O(s)} \rightarrow \text{Rh(s)} + \text{Rh(s)} + \text{O}_2$	5.329×10^{22}	-0.137	188.0	-
3	$\text{CO} + \text{Rh(s)} \rightarrow \text{CO(s)}$	$*5.000 \times 10^{-1}$	0.000	0.000	-
4	$\text{CO(s)} \rightarrow \text{Rh(s)} + \text{CO}$	1.300×10^{14}	0.295	134.0	ϵCO 47.00
5	$\text{CO}_2 + \text{Rh(s)} \rightarrow \text{CO}_2\text{(s)}$	$*4.800 \times 10^{-2}$	0.000	0.000	-
6	$\text{CO}_2\text{(s)} \rightarrow \text{Rh(s)} + \text{CO}_2$	3.920×10^{11}	0.315	20.51	-
7	$\text{NO} + \text{Rh(s)} \rightarrow \text{NO(s)}$	$*5.000 \times 10^{-1}$	0.000	0.000	-
8	$\text{NO(s)} \rightarrow \text{NO} + \text{Rh(s)}$	2.000×10^{14}	0.000	108.9	-
9	$\text{O(s)} + \text{C(s)} \rightarrow \text{CO(s)} + \text{Rh(s)}$	4.629×10^{23}	0.000	92.14	-
10	$\text{CO(s)} + \text{Rh(s)} \rightarrow \text{O(s)} + \text{C(s)}$	2.556×10^{23}	-0.000	174.8	ϵCO 47.00
11	$\text{O(s)} + \text{CO(s)} \rightarrow \text{CO}_2\text{(s)} + \text{Rh(s)}$	2.073×10^{25}	0.044	165.0	ϵCO 47.00
12	$\text{CO}_2\text{(s)} + \text{Rh(s)} \rightarrow \text{O(s)} + \text{CO(s)}$	1.231×10^{25}	-0.110	241.0	-
13	$\text{NO(s)} + \text{Rh(s)} \rightarrow \text{N(s)} + \text{O(s)}$	8.800×10^{23}	0.000	136.5	-
14	$\text{N(s)} + \text{O(s)} \rightarrow \text{NO(s)} + \text{Rh(s)}$	6.784×10^{23}	-0.046	234.7	ϵN 8.350
15	$\text{N}_2 + \text{Rh(s)} + \text{Rh(s)} \rightarrow \text{N(s)} + \text{N(s)}$	7.027×10^{15}	0.500	106.3	-
16	$\text{N(s)} + \text{N(s)} \rightarrow \text{N}_2 + \text{Rh(s)} + \text{Rh(s)}$	1.204×10^{22}	0.000	151.9	ϵN 16.70
17	$\text{O(s)} + \text{O(s)} \rightarrow \text{O}_2\text{(s)} + \text{Rh(s)}$	9.973×10^{22}	-0.427	257.8	-
18	$\text{O}_2\text{(s)} + \text{Rh(s)} \rightarrow \text{O(s)} + \text{O(s)}$	7.500×10^{22}	-0.000	164.8	-
19	$\text{O}_2\text{(s)} + \text{O(s)} \rightarrow \text{O}_3\text{(s)}$	6.883×10^{21}	0.000	163.0	-
20	$\text{O}_3\text{(s)} \rightarrow \text{O}_2\text{(s)} + \text{O(s)}$	1.468×10^{12}	0.000	190.5	ϵO_3 7.000 μO_3 0.7.00
21	$\text{N(s)} + \text{O}_2\text{(s)} \rightarrow \text{NO(s)} + \text{O(s)}$	6.280×10^{21}	-0.020	213.0	ϵN 8.350
22	$\text{NO(s)} + \text{O(s)} \rightarrow \text{N(s)} + \text{O}_2\text{(s)}$	1.093×10^{22}	-0.400	207.8	-

Table 6 The thermodynamic properties of surface species at 298.15 K

	Cp J/(K·mol)	H ₀ J/mol	S ₀ J/(K·mol)
Rh(s)	0.000	0.000	0.000
O(s)	14.37	-9.456 × 10 ⁴	26.99
CO(s)	23.77	-2.466 × 10 ⁵	57.82
C(s)	9.400	-6.946 × 10 ⁴	25.78
CO ₂ (s)	39.43	-4.168 × 10 ⁵	97.72
NO(s)	26.94	-2.001 × 10 ⁴	25.85
N(s)	12.96	-2.350 × 10 ⁴	3.660
O ₂ (s)	25.20	-9.719 × 10 ⁴	32.64
O ₃ (s)	39.57	-2.193 × 10 ⁵	87.47

For the reaction mechanism determined as described above, the thermodynamic properties of each surface species at 25°C are calculated and shown in Table 6. The value for Rh(s), which represents a vacant site, is used as a reference. Since the values of specific heat at constant pressure Cp and specific standard entropy S⁰ are positive for all species, thermodynamic consistency is achieved. Thus, it can be concluded that DETCHEM^{ADJUST} successfully worked.

4.5 Simulations on Light-Off Test

Figure 3 presents the simulation results for the four light-off test conditions described in Sect. 3.1. For the simulation of the light-off test after hydrogen reduction, the initial surface state was set to Rh(s)=1.0. For the simulation of the 1st light-off test after lean pretreatment, the initial surface state was defined based on the XPS analysis results [11]. For the 2nd and 3rd light-off simulations following lean pretreatment, the initial surface state was determined using the surface composition calculated by the model after the 1st and 2nd light-off tests. Under all conditions, although some discrepancies in the purification rate were observed, the overall light-off curve behavior was successfully reproduced through numerical simulation. The rise of the light-off curve was captured within a temperature range closely matching the experimental results. However, deviations in low-temperature conversion rates during the light-off test after lean pretreatment, discrepancies in CO conversion behavior after hydrogen reduction, and differences in NO conversion rates at high temperatures require further investigation.

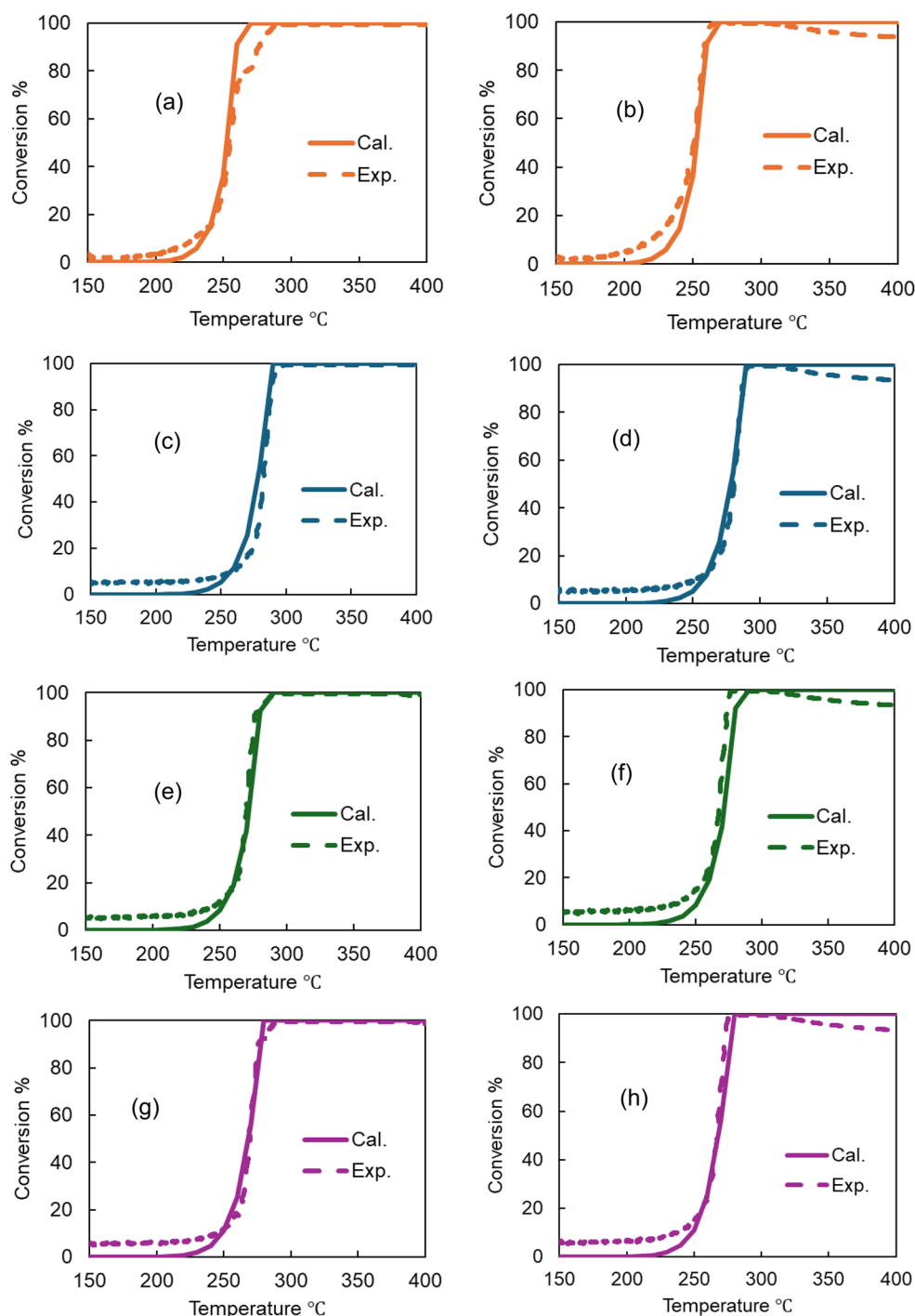
As shown in Fig. 4, the simulation successfully reproduced two key behaviors: (i) the light-off curve after lean pretreatment was delayed compared to that after hydrogen reduction, and (ii) when the light-off test was repeated following lean pretreatment, significant improvement was observed from the first to the second and third tests, while no noticeable difference appeared between the second and third tests. Therefore, this model can be considered capable of predicting the impact of oxide film formation and decomposition on Rh surfaces on purification performance.

Figure 5 shows the simulated changes in the surface state of the Rh catalyst during the light-off test. By comparing Figs. 4 and 5, the following interpretation can be made regarding the cause of the differences in light-off curve behavior due to experimental conditions. When comparing the state after hydrogen reduction with that after lean treatment, it is observed that, following lean treatment, O₃(s) partially covers the surface, reducing the proportion of active metal sites and thereby lowering the adsorption rates of CO and NO. Consequently, the purification reactions of CO and NO are delayed, and the light-off curve, which represents purification performance, shifts to higher temperatures. Furthermore, when comparing changes in surface species during repeated light-off tests after lean treatment, from the first to the third test, the oxide film formed under lean conditions gradually decomposes, reducing the coverage of the surface by the oxide film. As a result, CO and NO adsorption become easier, and the corresponding purification reactions proceed more effectively. Therefore, compared to the first light-off test after lean treatment, the light-off curve shifts to lower temperatures in the second and subsequent tests. The reason why there is smaller change between the second and third tests than between the first and second tests is that, during the first light-off test, almost all decomposable oxide films have already broken down, leaving an extremely small amount of oxide film to be further decomposed in the second test.

From Fig. 6 (a)–(d), it is evident that, aside from the differences in the proportion of oxide film covering the surface and the associated changes in reaction rate, the variations in surface species during light-off tests under each condition exhibit generally similar trends. Initially, the active sites on the surface are covered by CO(s) and NO(s). Next, NO adsorbed on the surface decomposes into N(s) and O(s), increasing the proportion of N(s) covering the surface. At the temperature range where N(s) and CO(s) begin to be converted into N₂ and CO₂ corresponding to the temperature at which the light-off curve rises in Fig. 5, N(s) and CO(s) decrease, and Rh(s) begins to increase. Thereafter, regions not covered by oxide films largely revert to metallic Rh. Under conditions where an oxide film is present, the proportion of O(s) increases as the oxide film decomposes, temporarily covering the metal surface; however, ultimately, both O(s) and O₃(s) decrease, and Rh(s) increases again.

Figure 7 summarizes the reactions considered for the first light-off tests after lean pretreatment. First, exposure to lean atmosphere leads to oxygen adsorption on the Rh catalyst surface, forming O(s) (Reaction No. 1). Subsequently, O(s) species react with each other to form O₂(s), and then the oxide film O₃(s) is produced (Reaction No. 17 and 19). During the light-off test, as the temperature increases from 150

Fig. 4 The comparison of light-off curves between experiments and simulations. CO (a, c, e, g) and NO (b, d, f, g) light-off curves after H₂ reduction (a, b), 1st (c, d), 2nd (e, f), and 3rd (g, h) light-off curve after lean pretreatment.



°C, only the adsorption reactions of CO and NO occur in the low-temperature range of 150–170 °C (Reaction No. 3 and 7). Above 170°C, purification reactions gradually begin (Reaction No. 6, 11, 13, 15), but up to 280 °C, the adsorption reaction rates exceed the surface reaction rates involved in purification, and metallic Rh(s) does not appear. Once

the temperature exceeds 280 °C, the surface reaction rates involved in purification surpass the adsorption rates, leading to further purification and an increasing fraction of metallic Rh on the surface. Additionally, above 350 °C, the decomposition of the oxide film O₃(s) by N(s) begins, slightly reducing the amount of O₃(s) present (Reaction No. 21).

Fig. 5 The comparison of simulated light-off curves depending on the conditions

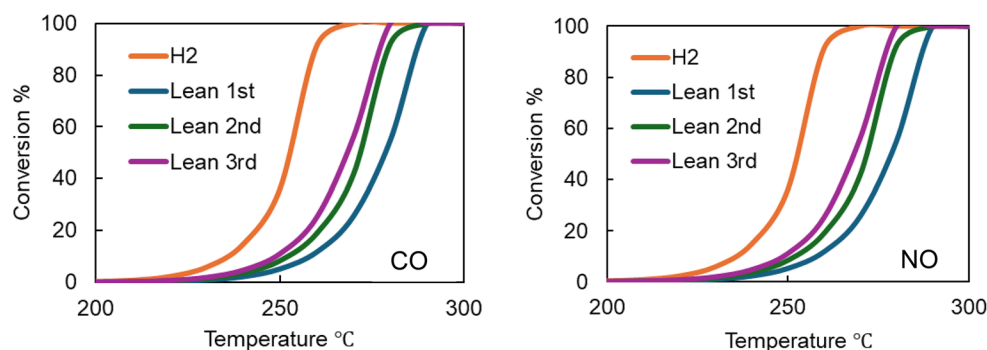
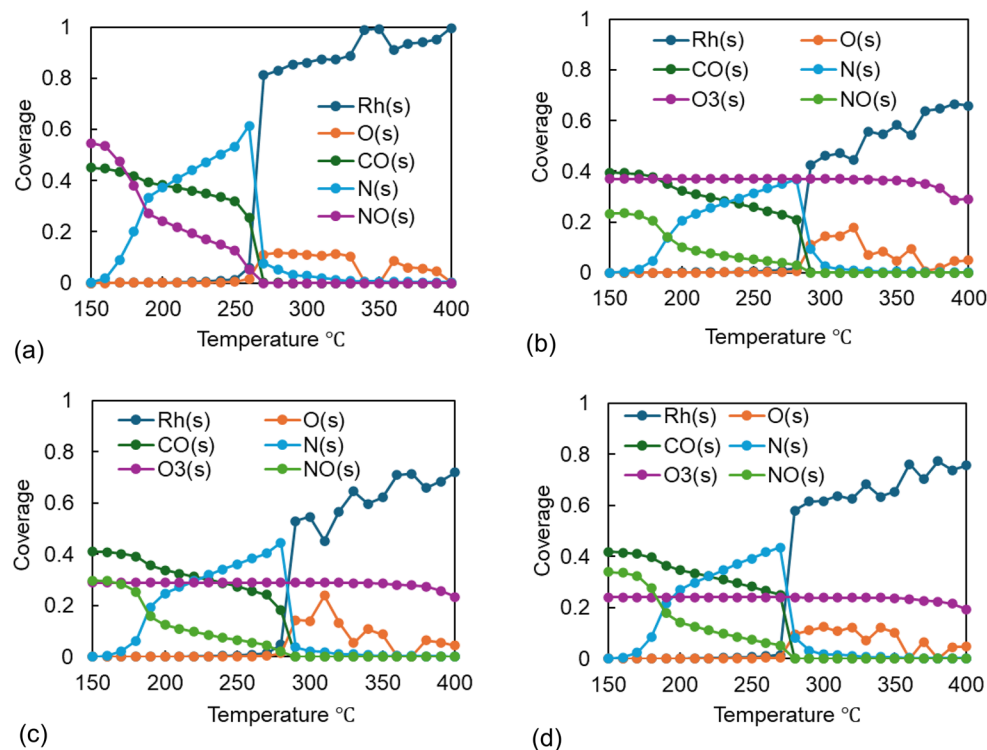


Fig. 6 Predicted coverage profiles of surface species during light-off after H_2 reduction (a), the 1st (b), 2nd (c) and 3rd (d) light-off after lean pretreatment



5 Conclusions

In this study, we experimentally investigated the effect of oxide film formation and decomposition on the Rh surface of a three-way catalyst on the CO oxidation and NO reduction characteristics. Furthermore, we introduced a thermodynamically consistent reaction scheme and performed numerical simulations that considered detailed surface reactions. This enabled us to reproduce the experimental results through calculations. Furthermore, we analyzed the surface state through calculations and obtained the following conclusions.

- Not only in the CO oxidation reaction but also in the NO reduction process, differences in pretreatment atmosphere affected the light-off performance. The light-off curve after pretreatment in a lean atmosphere shifted to

higher temperatures compared to that after hydrogen reduction treatment, with the temperature at which the purification rate reached 50% (T50) being approximately 30°C higher.

- After pretreatment in a lean atmosphere, when the light-off test was repeated three times, the second and third light-off curves started to rise at lower temperatures than the first light-off curve but never matched that obtained after H_2 reduction treatment. This suggests that only a part of the oxide film formed during lean atmosphere pretreatment was decomposed during the light-off test, and the surface didn't return to its fully metallic state.
- We reviewed part of the scheme in the model developed in previous studies and successfully constructed a model that maintains thermodynamic consistency by treating oxide film formation and decomposition as a two-step reaction.

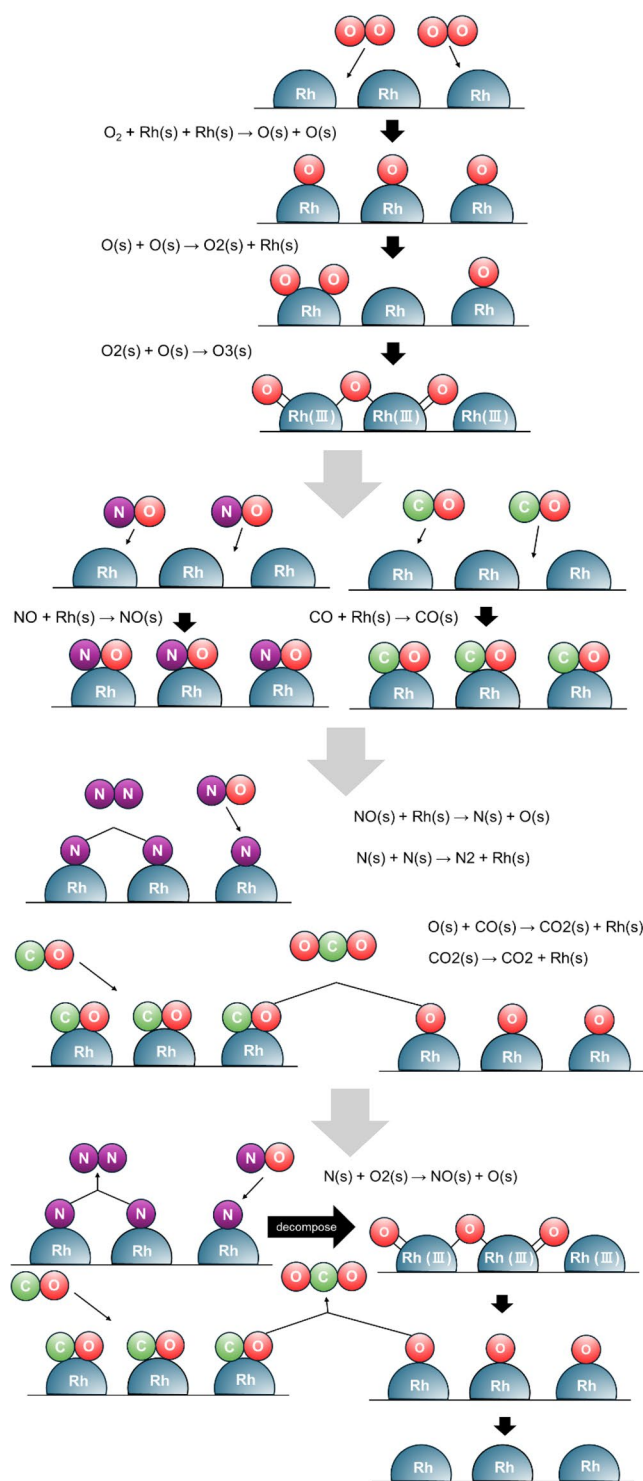


Fig. 7 Schematic of reaction process during 1st light-off after lean pretreatment

- By adjusting the parameters so that the decomposition rate of the oxide film depends on the amount of oxide covering the surface, we accurately represented the decomposition behavior of the oxide film during repeated

light-off tests after lean treatment and successfully reproduced the changes between the first and the second or third light-off curves through numerical simulation.

- Based on the numerical simulation results, it is inferred that the increase in light-off temperature caused by lean pretreatment is primarily due to the delayed reaction resulting from a higher oxide film coverage compared to H_2 reduction treatment. Furthermore, under lean pretreatment conditions, the oxide film is partially removed during the first light-off test, but even after repeated light-off tests, it was never decomposed beyond a certain proportion.
- Since $O_3(s)$ is smaller from the beginning during the second light-off test, the proportion of $Rh(s)$ is higher compared to the first test. As a result, the adsorption rates of $CO(s)$ and $NO(s)$ increase, improving CO and NO purification performance.

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Declarations

Ethics and Consent to Participate Not applicable.

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