

Search for Alloy Catalyst for Automobile Exhaust Gas by Means of Integrated Flow of Experiments, First-principles Calculation, and Materials Informatics

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ABSTRACT

A new integrated flow has been developed that makes it possible to efficiently search for alloy catalysts that reduce the amount of precious metals employed in catalysts for the purification of automotive exhaust gases. The distinctive feature of this flow is that it functionally integrates the properties of the conventionally performed test methods such as catalyst activation tests and X-ray photoelectron spectroscopy with those of first-principles calculations and materials informatics, performed using computers. First, experiments and first-principles calculations were used together in order to conduct an analysis of the nitrogen monoxide reduction reaction, and a density of state was set to function as an index of material performance. Next, the performance rank of binary alloy catalysts was predicted using first-principles calculations and materials informatics, with this density of state as the target variable. More than 10 binary alloy catalysts calculated as displaying performance in the top rank were actually synthesized and their performance was confirmed. The results showed that it was possible to create an alloy catalyst that displayed a higher level of performance than a catalyst using palladium, the main active metal in use in current catalysts, demonstrating the usefulness of the integrated flow.

1. Introduction

Increasingly urgent demands in relation to the preservation of the global environment in recent years have made it necessary to achieve further reductions in the quantities of CO₂, CO, HC, and NO_x present in exhaust gas emitted while vehicles are in operation. Effective responses to the reduction of CO₂ emissions during automobile operation are being promoted through automotive electrification, as exemplified by the use of hybrid vehicles⁽¹⁾. By contrast, the need to reduce emissions of CO, HC, and NO_x is being acknowledged by means of after-treatment using three-way catalysts⁽²⁾. Catalyst materials are employed in a form in which minute particles of precious metals such as platinum (Pt), palladium (Pd), and rhodium (Rh) are widely dispersed and loaded on the surface of an oxide such as alumina (Fig. 1). The inherent rarity of these precious metal resources makes them substances with a high procurement risk⁽³⁾. A reduction in the amount of use of precious metals is thus demanded in order to respond to future increases in the stringency of global automotive

exhaust gas regulations and increases in the number of automobiles sold in developing nations.

A variety of approaches have been taken from the perspective of effective use of the precious metals that have conventionally been used as the active species in catalysts, a typical example being the modification of the oxides that support the precious metals⁽⁴⁾. One of the aims of this is to maintain the precious metal particles on the surface of the oxide in a highly dispersed state even in environments such as automotive exhaust gas, in which temperatures are high and there is considerable fluctuation in the redox

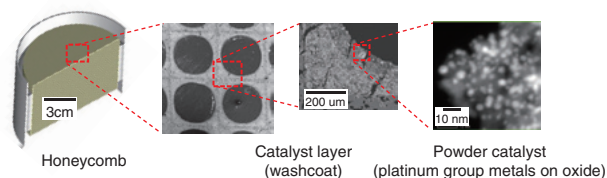


Fig. 1 Layout of catalyst material in exhaust system

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atmosphere. However, there is considered to be a theoretical limit to realizing increases in dispersibility. Another aim of these measures is to boost purification performance by means of the mutual interaction between the loaded metal and the oxide, known as the support effect⁽⁵⁾. There are, however, numerous unclear points regarding the mechanism to realize this function, and at present the effect also remains unclear. It will be challenging to further reduce the total amount of precious metals employed in exhaust gas purification catalysts through such catalyst oxide modification approaches alone.

Another approach that can be considered is to modify the active species themselves. While it is well known empirically that only precious metal elements are highly effective as active species, there has not been sufficient elucidation of the mechanism that causes only precious metals to function effectively. In addition, the development of materials has also not progressed in comparison to oxides, the reason being that because the catalytic reaction proceeds extremely rapidly, it has been considered that there were limits on the potential for elucidation of the mechanism through experimental methods alone. Thus, the search for new active species has, rather than basing itself on theory, mainly employed test methods that rely on previous experiments and findings, resulting in time-intensive material development.

The dramatic increase in computing power in recent years, however, has greatly changed the material research and development environment.

One of these changes has been the vigorous implementation of an approach to the elucidation of the reaction mechanism between gases and active metals involving the application of electronic structure analysis using first-principles calculations⁽⁶⁾⁻⁽¹²⁾. However, at present, the simulation of all of the complex catalytic reactions that occur simultaneously with redox reactions in gases in which there are numerous reaction gas components, such as automotive exhaust gas, necessitates enormous computation costs, making the process unrealistic. A means of restricting the targets of the computations is, therefore, necessary.

Another change is the burgeoning use of a method termed materials informatics, which uses machine learning (able to easily handle enormous amounts of information) to enable effective searches across wide ranges^{(13), (14)}. Using this method, it is possible to search for materials that are beyond the range of previous experience and findings if appropriate target and explanatory variables are prepared. In order to apply the method to the search for catalyst active species, however, it would be necessary to set target and explanatory variables that accord with the reaction mechanism.

Making use of the recent rapid developments in the materials research and development environment, the research discussed in this paper thus sought to create a search flow that integrated experiments, first-principles calculations, and materials informatics, while focusing on

the modification of catalyst active species, an area in which comparatively little progress can be considered to have been made. The research also sought to efficiently search for and verify alloy active species that would simultaneously allow the reduction of the amount of precious metals employed and maintain or increase purification performance.

2. Concept of Materials Search and Integrated Flow

The concept of the materials search under discussion was to utilize computing power to the greatest possible extent in order to realize the greatest potential reductions in the number of experiments, and conduct materials searches efficiently using first-principles calculations and materials informatics. The following integration flow was examined in order to realize this goal.

First, using experiments and first-principles calculations, densities of state are set as indices for materials searches. Next, repeated iterations of first-principles calculations and materials informatics are employed in order to narrow down the materials able to realize high performance. Finally, the candidate materials are actually synthesized, their performance is confirmed, and they are selected.

Because the number of standards that can be synthesized at one time in normal experiments is limited, when the range of a search is broadened, the number of synthesized materials and performance tests increases, necessitating more time. This represents an issue for experiments-based searches. Conducting the greater part of material screening using computers in this way helps to address this issue. In addition, with regard to the setting of calculation conditions, an issue for first-principles calculations, the reactions that correspond experimentally with purification performance are set as calculation conditions. For the setting of target and explanatory variables that accord with the reaction mechanism, an issue for materials informatics, densities of state linked to actual catalyst performance confirmed by experiments and first-principles calculations are set as target variables, and the basic chemical parameters of the elements are set as explanatory variables. By supplementing the issues of experiments using calculations and their issues in this way, the aim of the research was to attempt to help avoid divergence between experiments and calculations, and create a functionally integrated search flow.

Figure 2 shows a comparison of search flows. In the conventional search flow, high-performance materials are searched for by repeating material synthesis and catalyst activity tests. As a result, the time necessary for the search can increase in proportion to the increase in the search range [Fig. 2(a)]. By contrast, in the integrated flow under discussion, the materials search is conducted using calculations based on conditions restricted through the use of already synthesized materials, and only materials showing prospects for the realization of high performance are actually synthesized and tested for confirmation of

performance. As a result, it is possible not only to conduct searches over a wide range in a comparatively short period of time, but to reduce the number of materials that are actually synthesized to the greatest possible extent [Fig. 2(b)].

NO, which is said to be resistant to purification because the NO purification reaction is a reduction reaction and thus more thermodynamically disadvantageous than CO and HC oxidation reactions⁽¹⁵⁾, was made the subject of the research, and the NO-CO reaction, important to three-way catalyst performance, was focused on. In addition, the reaction was analyzed by applying experiments and first-principles calculations to the NO dissociative adsorption reaction, which is considered to be the most important reaction in the NO reduction reaction pathway^{(16), (17)}. It was decided that the density of state, the target variable for the materials search, would be controlled by alloying with an active metal as a method of actually changing and realizing this parameter. This research conducted a search for a binary system composition that would form the basis of the alloy.

Below, the details of concrete efforts implemented following the integrated flow proposed in this research are discussed.

- (1) Understanding the correlation between catalytic reactions and density of state in active metals through experiments

The correlation between NO reduction performance and the density of state of catalyst metals was experimentally confirmed using catalyst activity tests, adsorbed species analysis and electronic structure analysis.

- (2) Analysis of density of state in reactions using first-principles calculations

Using first-principles calculations, the density of state that contributed to the reaction was analyzed, and a

local density of state (LDOS) index was established as a target variable for a materials search using materials informatics.

- (3) Alloy search using materials informatics

With the LDOS index as the target variable, binary alloys that allow the realization of high performance were searched for through repeated iterations of smart materials informatics (SMI)⁽¹⁸⁾, which has a high predictive accuracy based on comparatively low amounts of data, and first-principles calculations.

- (4) Synthesis and characterization of binary system alloy catalysts

The binary alloy compositions shown by the calculations to be in the top range of performance were actually synthesized as alloy catalysts, and the state of alloying and the electronic structure were confirmed in tests.

- (5) Evaluation of performance of binary alloy catalysts

The actual performance of the binary alloy catalysts was evaluated in catalyst activity tests.

The following sections will discuss the research details of each of the five steps described above.

3. Materials Search Method and Results

3.1. Understanding the Correlation between Catalytic Reactions and Electronic Structure in Active Metals through Experiments

3.1.1. Test method

- (1) Catalyst synthesis method

Six types of single-metal catalysts were created using the impregnation method employing a normal aqueous solution. γ - Al_2O_3 was employed as the support oxide for all of the catalysts (Table 1).

- (2) Evaluation of catalyst performance

Catalyst activity tests were conducted using an atmospheric-pressure fixed-bed reactor employing a model gas. Catalyst weight was 100 mg, and the total gas flow rate was 400 ml/min. With regard to pretreatment, following reduction treatment at 500°C, catalyst performance was evaluated at 50°C-increments descending from 500°C. Evaluations were conducted using two reaction gas conditions: simulated exhaust gas conditions (Table 2), and NO-CO conditions that enabled evaluation of the typical reactivity of the NO reduction reaction for exhaust gas (Table 3).

- (3) Adsorbed species analysis

The adsorbed amount of isocyanate (NCO species), an index of the dissociation properties of NO, was measured. These measurements were conducted in a NO-CO consecutive reaction format using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). With regard to pretreatment, following reduction treatment at 500°C, the measurements were conducted at 200°C. The gas flow sequence was as follows: Following a flow of NO, a purge was conducted using N_2 ; next, following a

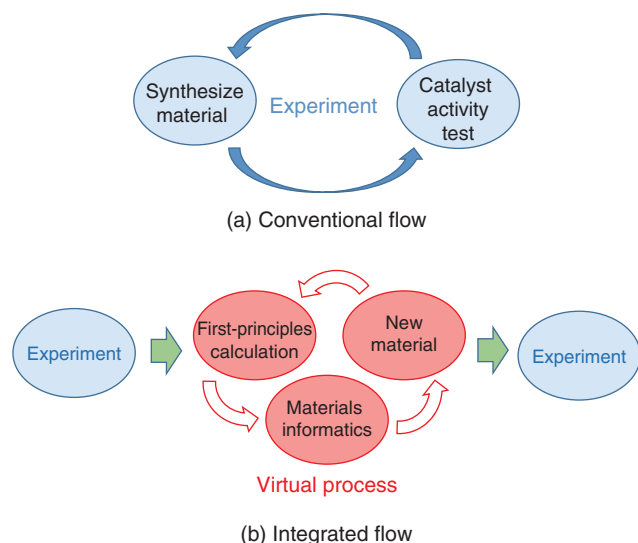


Fig. 2 Comparison of material search flows

Table 1 Sample catalyst

Catalytic active metal	Support oxide
Pd, Pt, Rh, Cu, Ag, Nd	γ -Al ₂ O ₃

Table 2 Simulated exhaust gas composition

Gases	Concentration
NO (ppm)	500
CO (ppm)	5000
C ₃ H ₆ (ppm)	400
H ₂ (ppm)	1700
O ₂ (ppm)	4900
CO ₂ (%)	14
H ₂ O (%)	10
N ₂	Balance

Table 3 NO-CO gas composition

Gases	Concentration
NO (ppm)	1000
CO (ppm)	1050
N ₂	Balance

flow of CO, a purge was conducted using N₂; peak strength measurements of NCO species were conducted at close to 2210 cm⁻¹.

(4) Analysis of catalyst electronic structure

X-ray photoelectron spectroscopy (XPS) was employed in the analysis of catalyst electronic structure. Measurements were conducted in a vacuum. The measurement conditions were as follows: MONO (Al) radiation source; voltage: 15 kV; current: 10 mA; the measurement energy band was from -15 eV to 40 eV. Samples were subjected to reduction treatment at 500°C as pretreatment, following which they were introduced to the measurement device in an inert gas environment without exposure to the atmosphere.

3.1.2. Experiment results

Because the material would ultimately be employed in an exhaust gas environment, it was first confirmed that there was no divergence between NO reduction performance under simulated exhaust gas conditions and NO-CO conditions in catalyst activity tests (Fig. 3). The results indicated that there was a correlation between the inclinations of the NO-reduction ratios under simulated exhaust gas conditions and NO-CO conditions. Given this, it was decided to proceed from this point on with the analysis under NO-CO conditions.

Next, Fig. 4 shows an image of the reaction pathway generated by dissociation, indicated as being an important reaction pathway in NO reduction. The dissociation

properties were evaluated using DRIFTS in order to experimentally investigate the correlation between the NO dissociation reaction and reduction performance. Because it was not possible to directly observe N atoms and O atoms, the adsorption strength of NCO species formed by the bonding of CO to dissociated and adsorbed N atoms was evaluated as the dissociation properties.

The results indicated a high correlation between the NO dissociation properties and the NO reduction ratio (Fig. 5).

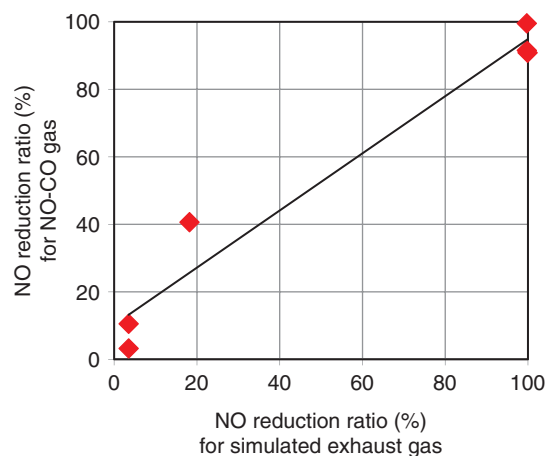


Fig. 3 Correlation between purification ratio for NO-CO gas and simulated exhaust gas

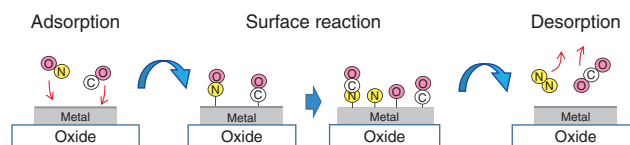


Fig. 4 Image of reaction path for NO reduction

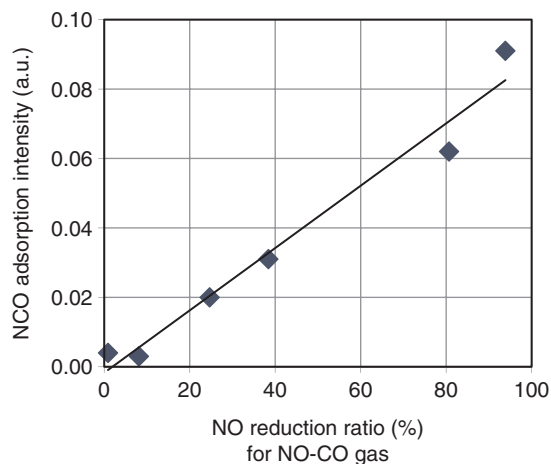


Fig. 5 Correlation between NO reduction ratio and NCO adsorption intensity

It was therefore confirmed that the NO dissociation reaction is an important reaction for the NO reduction reaction.

In the case of molecules that do not have paired electrons, such as NO, the driving force of the phenomenon of molecular dissociation is generally considered to be destabilization due to electron donation to antibonding orbitals (Fig. 6)⁽¹⁹⁾.

It is reasonable to assume that the source of these donor electrons is the catalytic metal into which the NO molecules are adsorbed. It was, therefore, considered that the dissociation reaction occurs as a result of electron donation from the catalytic metal to the NO molecules, and that the ease or lack thereof of this electron donation is dependent on the electronic structure of the catalytic metal. It was, therefore, conjectured that there would also be differences in the NO dissociation properties as a result of differences in the electronic structure of the catalytic metal (Fig. 7). The electronic structure of the catalyst valence band was therefore analyzed using XPS. The influence of the catalyst oxide was then subtracted, and the correlation between the electronic structure of the valence band of the catalytic metal alone (indexed valence value) and the dissociation properties of NO was investigated.

The results indicated a high correlation, as shown in Fig. 8, suggesting that electrons were donated from the catalytic metal to NO molecules.

Summarizing the results concerning NO reduction obtained in the series of experiments conducted up to this point:

- A correlation was obtained between the NO reduction ratio under simulated exhaust gas conditions and the NO reduction ratio under NO-CO conditions.

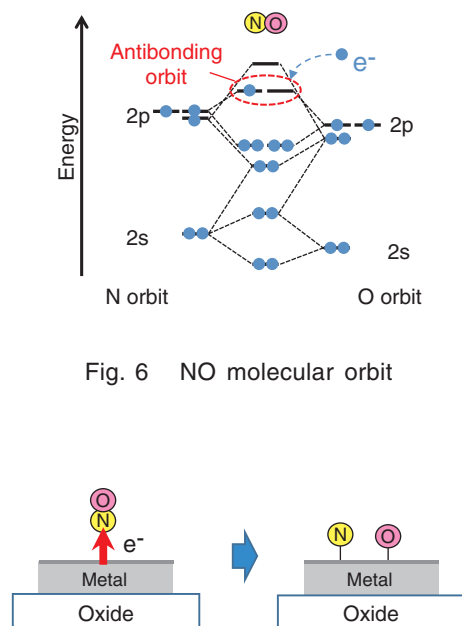


Fig. 6 NO molecular orbit

Fig. 7 Model of NO dissociation by electron donation

- It was confirmed that the NO dissociation reaction is an important reaction pathway for NO reduction, and that a correlation exists between the dissociation properties and reduction performance.
- A correlation between the dissociation properties of NO and the indexed valence value of the catalytic metal was confirmed.

Based on the results discussed above, it was considered that there was a correlative relationship between the electronic structure of the catalytic metal and NO reduction performance. It was therefore decided to conduct a detailed analysis of the density of state using first-principles calculations.

3.2. Analysis of Reaction Density of State Using First-principles Calculations

In order to provide theoretical backing for the observation that the NO dissociative reaction, which is important in the reduction of NO, occurs as a result of the donation of electrons from the catalyst metal, and to establish a search index for density of state in materials informatics, the electronic structure was analyzed using first-principles calculations.

3.2.1. Calculation method

The density of state in the NO dissociative adsorption process was analyzed using density functional theory (DFT), a representative first-principles calculation method⁽²⁰⁾. Table 4 shows the conditions for these calculations. The nudged elastic band (NEB) method⁽²¹⁾ was employed in the analysis of the process of transition. Table 5 shows the calculation conditions.

3.2.2. Density of state calculation model

Pd was employed as the representative metal in the calculation model. With regard to atomic position, NO

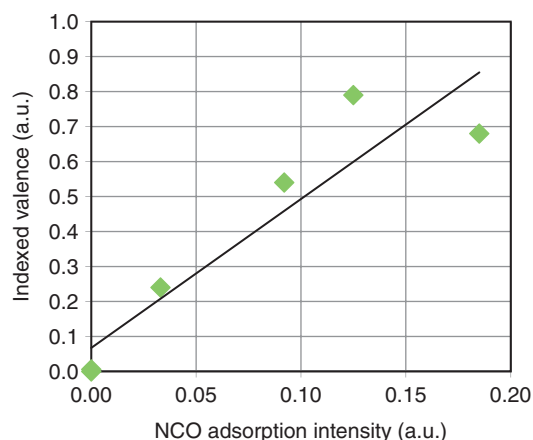


Fig. 8 Correlation between NCO adsorption intensity and indexed valence of catalytic active metal

Table 4 First-principles calculation conditions

Item	Detail
Software	Quantum espresso
Functional	PBE -GGA
Cutoff energy	35.0 Ry
K-points	$3 \times 3 \times 1$
SCF conv.	1E-07
Magnetism	Spin-unpolarized

Table 5 NEB calculation conditions

Item	Detail
Number of images	11
Optimize scheme	Quick-min
Path threshold	0.05 eV/Ang
Spring constant	0.1 a.u.

molecules were positioned on the outermost surface of the Pd (111) three-layer slab model as the initial state of the reaction, and N and O atoms were positioned as the final state of the reaction (total number of atoms: 38). For each positioning, the position in which adsorption would be stable was determined after conducting geometry optimization calculations. As a result, the state in which the NO molecule was adsorbed vertically into an fcc hollow site with the N atom and the Pd in contact was set as the initial state of the reaction (Image 0), and the state in which the O atom was dissociated and adsorbed into the adjacent fcc hollow site was set as the final state of the reaction (Image 10) (Fig. 9).

3.2.3. Calculation results

Figure 10 shows the distance between the N atom and the O atom from Image 0 to Image 10, following geometry optimization based on the NEB method.

These results indicate that the vertically adsorbed NO molecule collapses into the Pd surface, and from Image

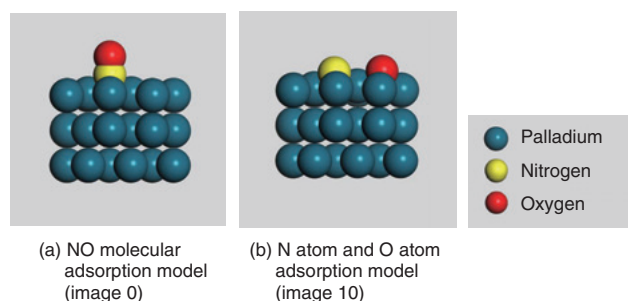


Fig. 9 NO adsorption model

5 onwards the distance between the N atom and the O atom gradually increases until dissociation finally occurs. The density of state during this process of transition was analyzed. The O atom was focused on in this analysis, as it was considered that because the O atom was at the furthest distance from the Pd surface in the initial state of the reaction and had been adsorbed into the Pd surface in the final state of the reaction, the change in density of state due to hybridization of orbitals would be greatest for this atom. Figure 11 shows a color map of the degree of change in LDOS in the p orbital of the O atom from Image 0 to Image 10. It was confirmed that there was a rapid increase in LDOS at close to 0 eV (in the white broken lines) from Image 6 onwards. This is considered to indicate that during the NO dissociation process, electrons were donated from the Pd to close to the Fermi level of the O atom (NO molecule).

Based on the results discussed above, it was considered from the changes in the position of the N atom and the O atom and the changes in density of state, that density of state close to the Fermi level contributed to the NO dissociation reaction. It was also considered that an alloy catalyst in which the density of state was high close to the Fermi level would promote more active electron donation to NO, boosting the dissociation properties of NO, with the result that it could be expected that NO reduction performance would ultimately increase. In this research, therefore, a particular energy band close to the Fermi level was specified, and LDOS within that range was employed as an index for the materials search.

3.3. Alloy Search Using Materials Informatics

The LDOS index value specified in Clause 3.2.3. was set as the target variable, and a binary alloy that would increase that value was searched for using SMI⁽¹⁸⁾, which offers good predictive accuracy even when the amount of data is

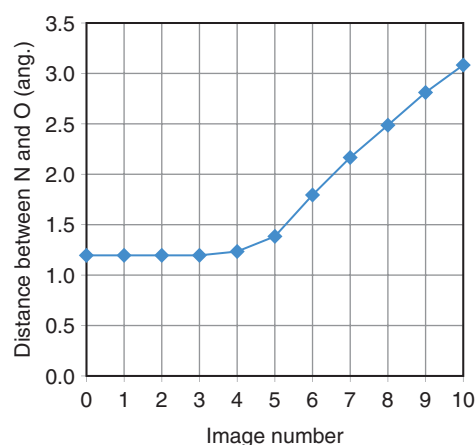


Fig. 10 Distance between N atom and O atom for each image

comparatively low. Because the purpose of calculations in the research under discussion was to reduce search time, and performance would ultimately be confirmed by testing, the calculation model for density of state was a face-centered cubic-based complete solid solution model. The composition ratio was a 1:1 atom ratio.

3.3.1. Density of state calculation model and calculation conditions

With regard to the positioning of the atoms, a bulk model [Fig. 12(a)] was formulated in which heteroatoms were uniformly arrayed in a complete solid solution. The calculation procedure was as follows: following the application of geometry optimization calculations using the bulk model, a six-layer slab model (total number of atoms: 24) was cut out of the (111) plane [Fig. 12(b)]. Geometry optimization calculations were then reapplied. Next, the LDOS for the two heteroatoms on the outermost surface in the specified energy band close to the Fermi level was calculated, following which the values that had been standardized by the value for Pd were set as indexed LDOS. The calculation conditions are shown in Table 6⁽²²⁾⁻⁽²⁴⁾.

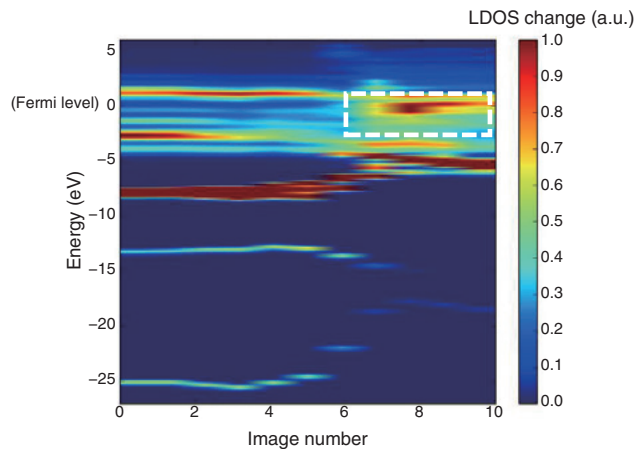


Fig. 11 Change in LDOS of oxygen p orbital during NO molecular dissociation process

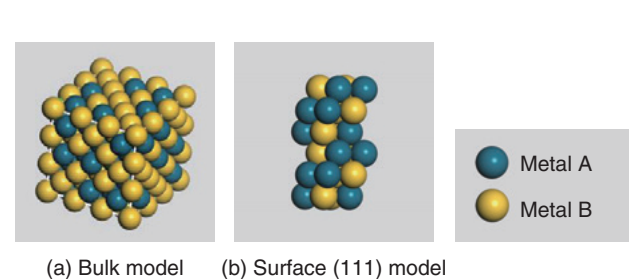


Fig. 12 First-principles calculation model

Table 6 First-principles calculation conditions

Item	Detail
Software	DMol ³
Functional	PBE -GGA
Basis set	DNP basis set
Core treatment	DFT Semi-core pseudopotential

3.3.2. Formulation of prediction model for LDOS index values

SMI was employed to formulate a prediction model with the LDOS index values for the two heteroatoms on the outermost surface as the target variable and the basic chemical parameters of the elements as the explanatory variables (Fig. 13).

In the first round of formulation of prediction models, LDOS index values for 48 single metal and 42 binary alloys (total: 90 types) were employed. Dozens of types of binary alloy predicted to have high LDOS index values based on the results were calculated and confirmed using DFT, after which the prediction model was updated by adding these as learning points. This active learning was conducted a number of times, increasing the accuracy of the prediction model. Ultimately, a prediction model was formulated based on LDOS index values for a total of 164 types of single metal and binary alloys.

3.3.3. Results of formulation of binary alloy prediction model

Figure 14 shows fitting results and leave-one-out cross-validation (LOOCV) results for the prediction model.

Given that the model was formulated using basic chemical parameters as the explanatory variables, the fitting results and LOOCV deviation are basically acceptable. Among the 2048 single-metal and binary alloys, excluding combinations with radioactive elements, gaseous elements and the like, the three precious metals Pd, Rh and Pt, which are already used in exhaust gas purification catalysts, each had an LDOS value in the top 30. Even when compared with empirical findings in this way, the LDOS calculation model and prediction model formulated in this research were demonstrated to possess a high degree of validity.

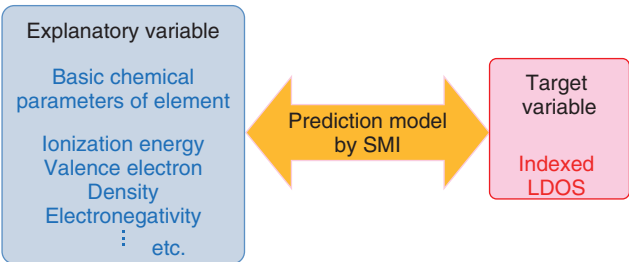


Fig. 13 Prediction model for indexed LDOS

3.4. Synthesis and Characterization of Binary Alloy Catalysts

Among the binary alloy compositions with high LDOS index values as indicated by the prediction model discussed in Clause 3.3.3., alloy catalysts that were considered synthesis candidates were synthesized, and the state of synthesis was confirmed.

3.4.1. Method of synthesis of binary alloy catalysts

In order to help preclude the extreme segregation of dissimilar metals in the alloy synthesis process or the phase-separated deposition that occurs in core-shell structure⁽²⁵⁾, particles that had been alloyed using the liquid phase reduction method⁽²⁶⁾, which creates the possibility for simultaneous deposition of dissimilar metals, were loaded onto γ -Al₂O₃. In the case of systems in which the reduction potential difference of the metallic elements was high and it was predicted that simultaneous deposition would not be easy, and systems which included elements with a higher reduction potential than the reducing agent, the alloys were synthesized by direct sputtering onto γ -Al₂O₃ using arc plasma⁽²⁷⁾.

3.4.2. Characterization of binary alloy catalyst

In order to confirm that alloy particles were present on the γ -Al₂O₃, structural analysis was conducted using X-ray diffraction (XRD), particle distribution was measured using scanning transmission electron microscope-energy dispersive X-ray spectroscopy (STEM-EDS), and an elemental analysis was performed for comprehensive judgment of the success of forming an alloy catalyst.

Figure 15 shows XRD measurement results for a PdCo alloy catalyst synthesized using the liquid phase reduction method as a typical example. The results of diffraction peak analysis showed that peaks do not appear at the diffraction angles that indicate Pd (111) and Co (111), while at the

same time, a peak indicating a PdCo solid solution alloy appears between those diffraction angles (shown by the arrow).

STEM-EDS analysis was applied to samples for which XRD structural analysis had confirmed the formation of a solid solution alloy. Figure 16 shows the results of electron microscopic observation and elemental analysis of the PdCo alloy catalyst.

From the high angle annular dark field (HAADF) image, in which contrast difference is obtained as a result of the atomic number, it was confirmed that metal particles were widely dispersed on the γ -Al₂O₃. Analysis of the state of elemental distribution using EDS mapping showed that Pd and Co are present in basically the same positions. Therefore, based on the results of XRD measurements and STEM-EDS observations, it was judged that PdCo was present on the γ -Al₂O₃ as alloy particles. The successful synthesis of a variety of alloy catalysts was judged in the same way. In addition, electronic structure measurements using XPS and measurements of indexed valence per concentration of loaded metal were conducted for the samples that were judged as alloy catalysts.

Table 7 shows the methods employed to synthesize the binary alloy catalysts that had been narrowed down as candidates by calculations, an indication of the success of synthesis, and the indexed valence values for the alloy catalysts.

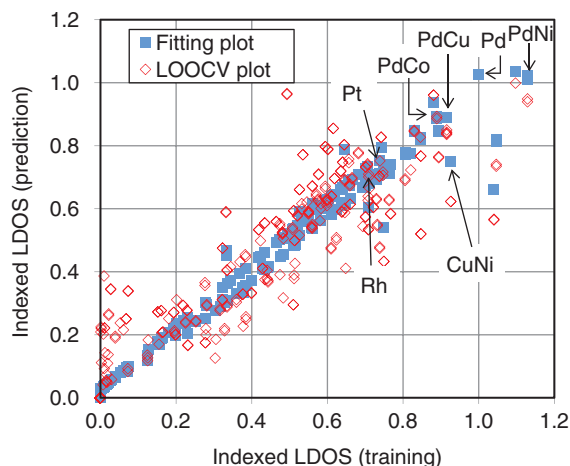


Fig. 14 Fitting result and LOOCV result

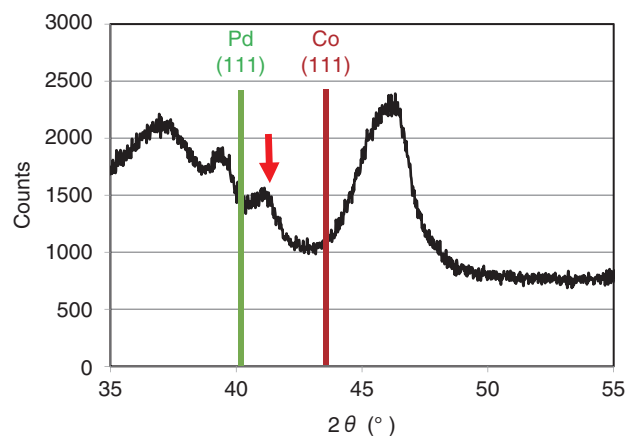


Fig. 15 XRD profile of PdCo alloy catalyst

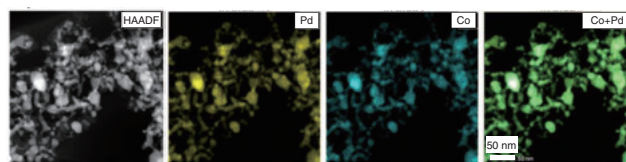


Fig. 16 STEM-EDS analysis of PdCo alloy catalyst

Table 7 Results of synthesis of alloy catalyst

Alloy system	Synthesis		Indexed valence (a.u.)
	Method	Success or failure	
Pd (Ref.)	Liquid phase reduction	S	26.1
PdNi	Liquid phase reduction	S	30.2
PdCu	Liquid phase reduction	S	12.2
PdCo	Liquid phase reduction	S	36.0
PdAu	Liquid phase reduction	S	6.2
PdAg	Liquid phase reduction	F	-
AuNi	Arc plasma	S	11.9
CuNi	Liquid phase reduction	S	9.1
CoNi	Liquid phase reduction	S	5.1
CoRe	Arc plasma	F	-
CoGe	Arc plasma	F	-
NiSn	Arc plasma	F	-
MoNi	Arc plasma	F	-
NiW	Arc plasma	F	-
CoMo	Arc plasma	F	-
NiRe	Arc plasma	F	-
CoCu	Arc plasma	S	11.2

4. Evaluation of Performance of Binary Alloy Catalysts

The performance of the alloy catalysts when new was evaluated under the NO-CO conditions employed in Clause 3.1.1. (2), and the correlation between the indexed valence value and catalyst performance at 300°C was evaluated (Fig. 17). Turnover Frequency (TOF), as expressed by Eq. (1) below, was employed as the index of catalyst performance. Note that the reaction surface, S , was calculated from the actual amount loaded and the average particle size for each alloy catalyst.

$$T.O.F. (\text{mol/sec} \cdot \text{m}^2) = A (\text{mol/sec}) / S (\text{m}^2) \quad (1)$$

A : Reaction molecule amount per second

S : Reaction surface

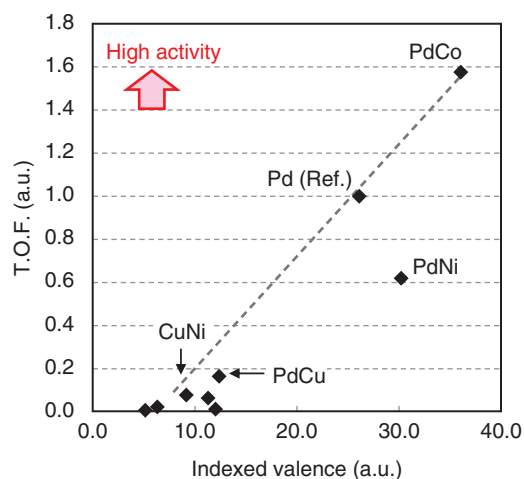


Fig. 17 T.O.F. against indexed valence for various alloy catalysts

The results showed that, as predicted, reduction performance tended to be greater in alloy catalysts with higher indexed valence values. In particular, the PdCo alloy catalyst displayed a level of performance approximately 1.6 times greater than a Pd catalyst (Ref.). The performance of the synthesized PdCo catalyst was therefore also evaluated under the simulated exhaust gas conditions employed in Clause 3.1.1. (2). The results are shown in Fig. 18.

Despite the fact that its Pd content was approximately two-thirds that of a Pd catalyst (Ref.) by weight ratio, its reduction performance exceeded that of the Pd catalyst in the 300°C-400°C range. This indicated that it had been possible to search for and verify the performance of an alloy catalyst that used a reduced amount of precious metals while also maintaining or increasing reduction performance, as per the initial target.

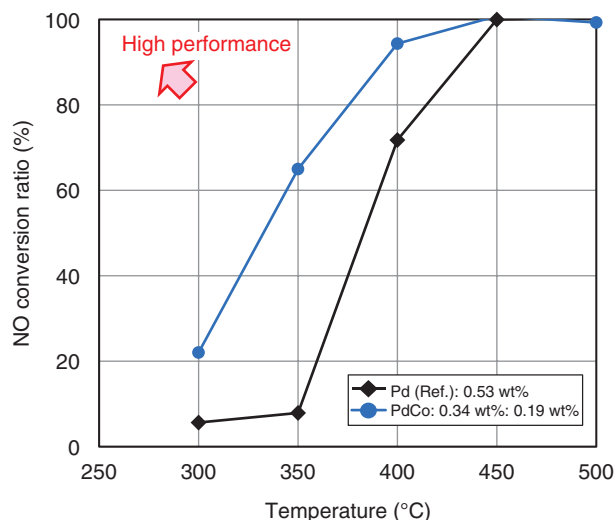


Fig. 18 Results of performance evaluation on condition of simulated exhaust gas composition

5. Conclusion

(1) A materials search flow that functionally integrates experiments, first-principles calculations and materials informatics was created, and its effectiveness was confirmed. The main points of this research are as follows:

- Experiments showed that correlations exist between NO reduction performance and NO dissociation properties, and between NO dissociation properties and the electronic structure of the valence band of the catalyst metal.
- Using first-principles calculations, an analysis of the density of state that contribute to the NO dissociation reaction was conducted, and LDOS in a specified

energy band close to the Fermi level was established as an index for materials searches.

- It was possible to efficiently search for binary alloy compositions that could realize high performance by conducting repeated iterations of materials informatics and first-principles calculations with indexed LDOS as the target variable.
- (2) A binary alloy identified by the materials search flow developed in this research falling in the top level of performance was synthesized, and a PdCo catalyst using 30% less Pd while realizing a higher level of performance than a Pd catalyst was created.

The basic concept of the integrated flow employed in this research is not restricted to catalyst materials but can be broadly applied, and its use in relation to a variety of materials searches can be expected in the future.

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