

Elucidation of Hydrocarbon Purification Mechanism of Catalyst for Lean Burn Engine Using Surface Analysis and Ab-initio Calculation with Large-scale Cluster Model

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ABSTRACT

When a platinum supported acidic support catalyst is used as a hydrocarbon purification catalyst for lean burn engines, it shows a high level of purification performance. In order to elucidate the causal factors, the surface state of the platinum particles was analyzed by an X-ray absorption near-edge structure analysis and ab-initio calculations, with a density functional theory using a large-scale cluster model and slab model, were carried out. The results showed that platinum particles retain a metallic state when acidic support is used. It was also found that there is a distribution of charge in the platinum particles, and when platinum atoms in proximity to the support are positively charged, they are in a state that tends to resist the adsorption of oxygen. It was found from these results that the high level of purification performance of acidic supported platinum is due to the electronic activity of the acidic support, which helps to prevent oxygen adsorption on the surface of platinum in proximity to the support so that the catalyst yields high activity with respect to paraffin.

1. Introduction

The reduction of CO₂, which is said to be a greenhouse gas, is an urgent issue for humankind. In order to reduce the CO₂ emitted from automobiles, it is important to raise the thermal efficiency of the engine. Attention is being focused on lean burn engines for this purpose. Honda has reported research on homogeneous lean charge spark ignition (HLSI) as one solution^{(1),(2)}.

In the lean exhaust gas atmosphere that accompanies lean burn, however, the three-way catalyst that is normally used in a stoichiometric atmosphere faced the issue of reduced efficiency in purification not only of nitrogen oxides (NO_x), but also of hydrocarbons (HC). Figure 1 shows the HC concentration and HC composition of stoichiometric and lean exhaust gas^{(3),(4)}. It is apparent that the lean exhaust gas has a higher HC concentration, with a particularly high proportion of paraffin. Figure 2 shows the temperature characteristics of HC oxidation reactions. The purification of paraffin occurs at a higher temperature than olefin and aromatics, indicating that purification does not occur readily. These factors are thought to cause a reduction in purification efficiency in a lean atmosphere.

The authors have determined that a platinum supported acidic support catalyst is effective for paraffin oxidation reactions^{(3),(4)}. Figure 3 shows a conceptual image of the reaction in a platinum supported acidic support catalyst. Among the precious metals, platinum is known to yield high activity in paraffin oxidation reactions. In this scheme, paraffin and oxygen are adsorbed onto the surface of the platinum particles, where they react with CO₂ and H₂O and are desorbed. In a lean atmosphere there is an excess

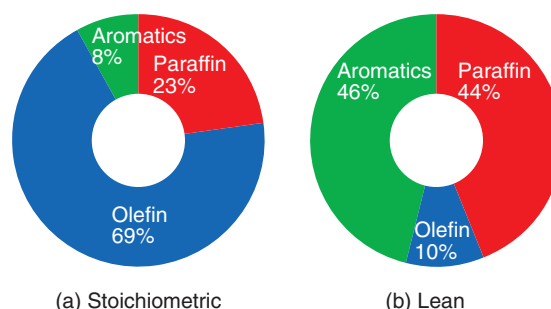


Fig. 1 HC composition in exhaust gas (HLSI, Ne: 1500 rpm, BMEP: 450 kPa)

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of oxygen relative to a stoichiometric atmosphere, so that oxygen is adsorbed onto the platinum surface, as shown in Fig. 3(a), and by covering the surface, it blocks the adsorption of paraffin and the reactivity is reduced. It was found, however, that when a high acidity material is used as a support for the platinum, it yields a higher level of paraffin oxidation activity. It has been inferred that when an acidic support is used, the electron-withdrawing effect of the acidic support causes the platinum particles to become electron deficient as shown in Fig. 3(b) so that the strength of the bond between the platinum surface and oxygen is reduced. This limits coverage of the platinum surface by oxygen and allows the paraffin and oxygen on the platinum surface to react more readily. However, the electron-withdrawing effect on the platinum caused by the acidic support and the limiting effect on oxygen adsorption by the platinum surface did not have sufficient detailed analysis or theoretical research. The present study is therefore founded on a research concept that combines an experimental approach in the form of surface analysis and so on together

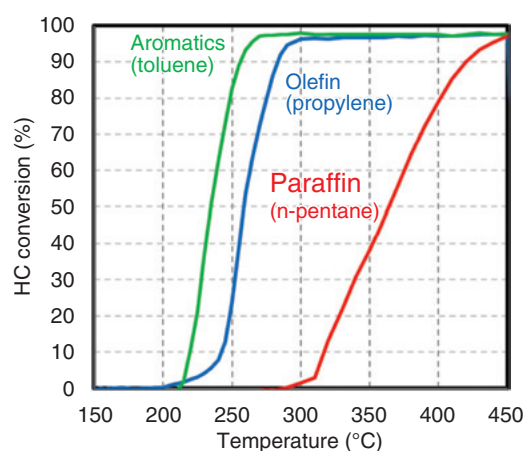


Fig. 2 Oxidation characteristic of HC (Catalyst: Three way catalyst, Aging: 750°C, Evaluation: O₂ 7%, HC 1200 ppm, CO 3000 ppm, NOx 70 ppm, CO₂ 8%, H₂O 7%)

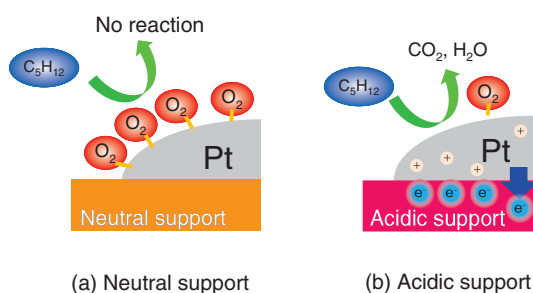


Fig. 3 HC purification mechanism of Pt supported catalyst

with a theoretical approach using ab-initio calculation for the purpose of substantiating the mechanism of high activity in a platinum supported acidic support catalyst that efficiently purifies paraffin.

2. Research Concept

The research conducted for this paper applied the following concept to the mechanism of high activity in a platinum supported acidic support catalyst that efficiently purifies the paraffin in lean burn exhaust gas.

Figure 4 shows a conceptual image of the configuration of a platinum supported acidic support catalyst. The catalyst material has an acidic oxide support, the surface of which supports platinum particles. This catalyst material is coated on a honeycomb surface and is used as a lean burn exhaust gas purification catalyst.

In order to obtain corroboration for the inferred scheme of reaction to the platinum supported acidic support catalyst, as shown in Fig. 3, three types of support material with different acidity were used as model materials. These three were SiO₂, Al₂O₃, and MgO. These were then used in the methods given as (1) to (3) below, and that evaluation of activity, analysis of material properties, and theoretical computation were conducted in a comprehensive examination of the matter.

(1) Evaluation of platinum supported catalyst activity

The activity is measured by using the reaction rate obtained for each catalyst through paraffin oxidation reaction tests, together with the platinum surface area obtained by CO adsorption amount measurement, to calculate the reaction rate per platinum atom.

(2) Clarification of the mechanism of high activity by analysis of material properties

The acidity of each support is determined by using ammonia temperature-programmed desorption (NH₃-TPD) to calculate the surface acid score of each support material. For the platinum supported catalyst, the amount of oxygen adsorption on the platinum surface is measured

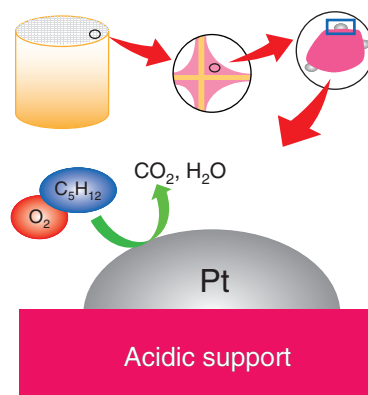


Fig. 4 Pt supported catalyst configuration

using O₂-TPD. Next X-ray absorption near edge structure (XANES) analysis is used to examine the electron state of the platinum particles. These are taken together to infer the causal factors for the activity difference measured in (1) from the influence that support acidity has on the platinum particles and platinum surface state.

(3) Corroboration of inference by theoretical computation

Calculations are made of the electron state of the oxygen adsorption characteristics using a large-scale platinum cluster model for each material and a platinum slab model that has the electron state altered deliberately. In this way, theoretical corroboration is obtained for the influence that the support acidity found in (1) and (2) has on activity and material properties.

For this research, the measures to calculate electron states using the large-scale platinum cluster model in (3) are of particular interest. The electron density of metals can be calculated by ab-initio calculation, and this method has been commonly used with automobile catalysts⁽⁵⁾,⁽⁶⁾. It does involve a computation cost, however, so there are limits on the number of atoms and calculations for structures combining multiple elements presented challenges. Consequently, there were few examples of investigation into calculations of support models with metal particles of a diameter, making them the same size as an actual catalyst⁽⁷⁾,⁽⁸⁾. For this paper, by contrast, the use of more efficient modeling techniques and the expansion of computer capabilities have made it possible to calculate the model for a structure of several hundred atoms supporting a large-scale platinum cluster. Therefore, it was decided to engage in calculations with cluster sizes more closely approximating reality.

On the other hand, ab-initio calculation of the oxygen adsorption state on a platinum surface was carried out without using a large-scale cluster model, which involves significant computation cost. The calculation was carried out instead using a platinum slab model to simulate the charge state on the platinum cluster surface. In this case, the slab model refers to a plate-shaped model with a specific index surface for the outermost surface and having a periodic boundary. Oxygen molecule adsorption is a phenomenon that occurs locally on the platinum metal surface. Therefore, an attempt was made to obtain calculation results more efficiently and in a shorter time by having the slab model represent only the atoms in those places considered likely to have a particularly large influence on adsorption.

The above research concept was used to elucidate the mechanism of high activity in a platinum supported acidic support catalyst used as an HC purification catalyst in a lean burn engine.

3. Experimental and Computational Methods

3.1. Samples

The platinum was supported by support material of different acidity and used as a platinum supported catalyst.

Table 1 Oxide materials

Type	Support material
Acidic oxide	SiO ₂
Neutral oxide	Al ₂ O ₃
Basic oxide	MgO

Table 2 Model gas composition

	Concentration
CO (ppm)	3000
HC (ppmC)	1200 (n-C ₅ H ₁₂)
NO (ppm)	70
O ₂ (%)	7
CO ₂ (%)	8
H ₂ O (%)	7

For the acidic support material, SiO₂ was used; for the neutral support material, Al₂O₃ was used; and for the basic support material, MgO was used (Table 1). Each support material was impregnated with platinum nitric acid solution, evaporated to dryness, and dried in an atmosphere at 150°C for 15 hours. It was then calcined in an atmosphere at 500°C for two hours and used as catalyst material. For analysis, support material powder and catalyst powder were used. For reaction testing, the catalyst material coated on cordierite honeycomb was used. The honeycomb had 900 cells, a thickness of 2.5 mils, a diameter of one inch, and a length of 30 mm.

3.2. Reaction Test Method

The purification performance evaluation of the catalyst was carried out using a model gas reactor. The composition of the model gas is shown in Table 2. It has a space velocity of 100000 h⁻¹. While the catalyst was exposed to the model gas flow, it was heated from room temperature to 400°C. The catalyst exit gas was analyzed and the purification rate before and after the catalyst was calculated. The catalyst was used after hydrothermal aging at 750°C for 20 hours.

3.3. Analysis Method

3.3.1. Measurement of number of atoms on platinum surface

The number of atoms on the platinum surface was measured by the CO adsorption amount. Pretreatment consisted of heating to 400°C in a flow of helium gas, followed by keeping at a constant 400°C in an H₂ atmosphere for 15 minutes. The temperature was then lowered to an ambient temperature in a flow of helium gas, after which a CO pulse of 200 mm³ was injected three time or more until the exit CO concentration was stable. The adsorption amount was then measured.

3.3.2. Acidity measurement

The evaluation of acidity was carried out using NH_3 -TPD. This method evaluates acidity according to the characteristic whereby a larger adsorption amount of NH_3 , which is a base, indicates higher acidity. The NH_3 desorption amount was measured after first heating the sample to 500°C in a helium atmosphere for 60 minutes and then exposing it to a flow of 0.5% NH_3 at 100°C for 60 minutes, following which it was heated from 100°C to 600°C in a flow of helium. After this pretreatment, the NH_3 desorption was measured using a quadruple mass spectrometer.

3.3.3. Oxygen adsorption amount measurement

Measurement of the oxygen adsorption amount was carried out using O_2 -TPD. Pretreatment consisted of holding the sample at 500°C in an oxidizing atmosphere for 60 minutes. It was then exposed to a flow of helium and heated from ambient temperature to 900°C , after which the oxygen desorption amount was measured using a quadruple mass spectrometer.

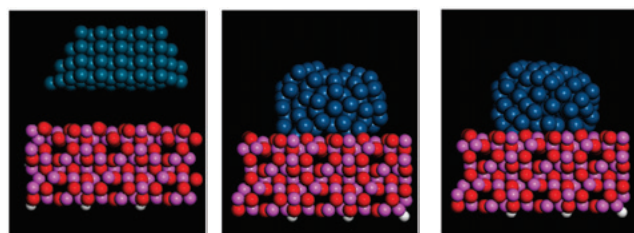
3.3.4. Electron state analysis

XANES measurement was carried out to examine the electron state of the platinum particles. The analyzing device was the BL-11 line at the Kyushu Synchrotron Light Research Center (case number 1606044G). An Si(111)2 crystal spectrometer and an ion chamber detector were used. Measurement was carried out in vacuum by the transmission method to obtain Pt-III Edge spectra for analysis.

3.4. Ab-initio Calculation Method

3.4.1. Creation of large-scale cluster model

Theoretical calculation of the electron state necessitates modeling of the platinum support state on the support. It is conceivable that, in creating a large-scale cluster model, the atomic arrangement and electron state of the stable structure that is finally obtained through ab-initio calculation may end up in a state that depends on the initial atomic arrangement. Therefore, the initial atomic arrangement, as shown in Fig. 5(a) and (b), does not have the platinum atoms arranged manually. The procedure used here to create the model instead set up the atomic arrangement in a broad



(a) Initial (b) After MD (c) After ab-initio

Fig. 5 Cluster model of Pt supported catalyst

Table 3 MD calculation conditions

Item	Detail
Software	LAMMPS
Potential	Lennard-Jones
Simulation time, Time step	500.0 ps, 1.0 fs
Ensemble condition	NVT

Table 4 Ab-initio calculation conditions

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

manner using classical molecular dynamics (MD) so that the energy field between the atoms could be considered on a macro scale. After that, the stable structure was calculated in detail from the ab-initio calculation, which takes quantum mechanics into consideration. Then the model was completed as shown in Fig. 5(c).

The above method combining MD calculation and ab-initio calculation was employed because it was reasoned that this would enable more efficient modeling of a platinum support state that is closer to reality. Specifically, in order to simulate the state of platinum particles approximately 1 nm in diameter, supported on an oxide support, a model was created in which there is a platinum cluster consisting of approximately 100 atoms on an oxide support with about five layers.

3.4.2. Molecular dynamics calculation

The calculation was carried out with the atoms of the oxide support in a fixed state and an initial velocity given only to the platinum atoms supported. Table 3 shows details of the calculation conditions.

3.4.3. Ab-initio calculation

For this paper, the electron state of the platinum was analyzed using ab-initio calculation based on density functional theory. For this purpose, a platinum support cluster model was used to analyze the electron state of the supported platinum, and a platinum slab model was used to analyze oxygen adsorption on the platinum. For calculation of the platinum support cluster model, structure optimization calculation was carried out with that half of the platinum on the side not supported by the oxide support in a fixed state. For the platinum slab model, a model of 32 atoms in eight layers was adopted. The oxygen molecules and the three layers of platinum atoms from the outermost surface down were subjected to structure optimization calculations. All of the calculations were carried out under the conditions shown in Table 4⁽⁹⁾⁻⁽¹¹⁾.

4. Results of Experiment and Calculation

4.1. Evaluation of Activity of Platinum Supported Oxide Catalyst

Testing was performed of the paraffin purification performance of platinum oxide catalyst with platinum supported on oxides of differing acidity, and the amount of platinum on the surface was calculated from measurements of the CO adsorption amount. Turn over frequency (TOF) was used as an index for purification activity. As shown in Eq. (1) below, the TOF is a figure that indicates the number of reactions per unit of time per atom of active metal. It is commonly used as an index of activity.

$$\text{TOF(/sec)} = \frac{\text{Reaction rate (mol/sec)}}{\text{Amount of active metal on surface (mol)}} \quad (1)$$

The reaction rate at 300°C and the surface platinum amount in the purification performance evaluation results were used in Eq. (1) to determine the TOF. Those results are shown in Table 5. It was observed from these results that the catalyst using an acidic support, which was Pt/SiO₂, had the highest TOF. Considering also that the Pt/SiO₂ catalyst had a surface amount of platinum that was one order of magnitude smaller than the other two catalysts, it could be inferred that progressive aggregation of the platinum particles is taking place. Despite that, however, it was found that the platinum atoms on the surface maintained a high level of activity.

4.2. Inference of Causal Factors of High Activity According to Analysis of Material Properties

4.2.1. Examination of oxide support acidity

The acidity of each oxide was evaluated using measurements of the NH₃ adsorption amount and the results are shown in Table 6. As anticipated, these results confirmed that the NH₃ adsorption amount is greater in descending order of SiO₂, Al₂O₃, and MgO, and that the acidity is greater in this order.

4.2.2. Characteristics of oxygen adsorption on the platinum surface

It was inferred that the reason for the higher paraffin purification performance of acidic support, as shown in Fig. 3, was that oxygen adsorption on the platinum surface was inhibited. The oxygen adsorption amount was therefore measured by O₂-TPD in order to ascertain the characteristics of oxygen adsorption by the platinum oxide catalyst. The results are shown in Table 7. The oxygen adsorption amount was greater in descending order in Pt/MgO, Pt/Al₂O₃, and Pt/SiO₂. In other words, this suggests that the catalyst using SiO₂ with its higher acidity as a support has the effect of reducing oxygen adsorption on the platinum. According to this effect, support material with higher acidity would have a correspondingly smaller amount of adsorbed oxygen on the platinum surface. It was inferred

Table 5 Calculation of TOF in Pt supported catalyst

Catalyst	Conversion (%)	Pt amount (μmol)	TOF (/sec)
Pt/SiO ₂	48.0	2.4	0.44
Pt/Al ₂ O ₃	70.0	29.0	0.04
Pt/MgO	30.0	28.0	0.02

Table 6 Amount of NH₃ adsorption in NH₃-TPD

Material	NH ₃ ads. (μmol/g)
SiO ₂	63
Al ₂ O ₃	23
MgO	2

Table 7 O₂ adsorption amount on Pt in O₂-TPD

Catalyst	O ₂ ads. (μmol/g)
Pt/SiO ₂	4
Pt/Al ₂ O ₃	12
Pt/MgO	50

that this would allow paraffin to be more readily adsorbed on the platinum surface, advancing the oxidation reaction so that the TOF was higher.

4.2.3. Platinum electron state analysis

It was inferred that oxygen adsorption on the platinum was inhibited due to the different electron state of the platinum particles on the various oxides. XANES measurement was therefore carried out. At this time, measurements were also made of platinum foil for the purpose of comparison of the metal state and measurements of a piece of PtO₂ for the purpose of comparison of the oxidation state. The results are shown in Fig. 6. It was apparent from these results that the peak representing the platinum on SiO₂ is closest to the peak for platinum foil. The peak location shifts increasingly in the direction of the PtO₂ piece with Al₂O₃ and MgO, in that order. In other words, this indicated that platinum on the SiO₂ is closest to

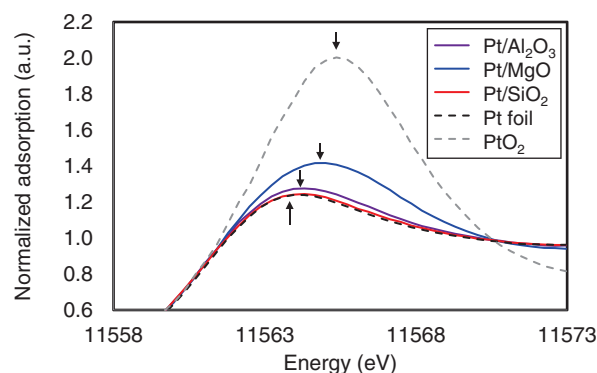


Fig. 6 XANES spectrum of Pt supported catalyst

the metallic state. This further confirmed that the Pt/SiO₂ catalyst inhibits oxygen adsorption on the platinum surface.

4.3. Corroboration of Inferences Based on Theoretical Computation

4.3.1. Ab-initio calculation based on cluster model

An analysis of material properties suggested that the electron state of platinum particles influence the enhanced performance of oxide catalysts. In order to clarify the kind of electronic influence the support has on platinum particles, therefore, calculations were made of the electron state of a cluster model with a platinum cluster arranged on an oxide support. Figure 7 shows the cluster models for each oxide. In every case, the platinum cluster was a globular form in a stabilized state supported on the oxide support. Due to the differences in support material, however, the platinum clusters ended up taking different shapes. It is inferred that this is due to the different ways in which the support materials and platinum clusters interact.

In order to ascertain the electron state of the platinum clusters in these platinum cluster models, the clusters as a whole were subjected to Hirshfeld charge analysis. The results are shown in Table 8. It was found from these results that the positive charge amount is higher in SiO₂, Al₂O₃, and MgO, in decreasing order. In other words, this can be interpreted to mean that when the support has higher acidity, the platinum cluster will have an electron deficiency. The cause of this could be that the acidic oxide support has greater electron-withdrawing force than other oxides.

Further calculation was also made of the electron state of each individual atom making up the platinum cluster and the charge distribution within the platinum cluster was examined. Figure 8(a) to (c) shows the charge distribution in the platinum clusters. The vicinity of the XY plane in the figures is the point of contact with the support oxide. The charges of all the atoms within the platinum cluster in the model were color coded and plotted on their coordinates. In every figure from (a) to (c), the charge distribution within the platinum cluster is uneven. The positive charges were concentrated in the vicinity of the point of contact with the support while the negative charges were concentrated in the upper part of the cluster. The positive charges were localized in a particularly conspicuous manner in the vicinity of the

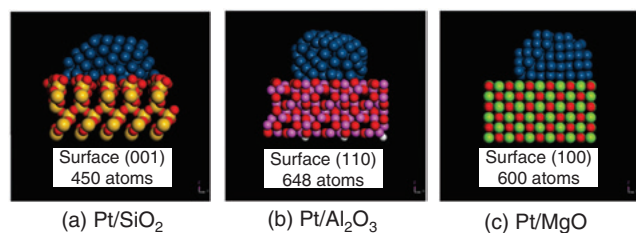


Fig. 7 Cluster models of Pt supported catalyst

Table 8 Charge of Pt cluster

	Pt/SiO ₂	Pt/Al ₂ O ₃	Pt/MgO
Total charge of Pt cluster	5.93	3.1	0.19
Maximum + charge	0.32	0.31	0.06
Maximum - charge	-0.02	-0.04	-0.05

point of contact with the support in the charge distribution for the platinum cluster on Pt/SiO₂ shown in Fig. 8(a). It can be inferred that this occurs because the SiO₂ is an acidic support with an electron-withdrawing effect that results in electrons travelling from the platinum to the support in the vicinity of the point of contact with the support, so that the lower part of the platinum cluster instead becomes positively charged.

It was found from the above that ab-initio calculation based on the cluster model showed the support with higher

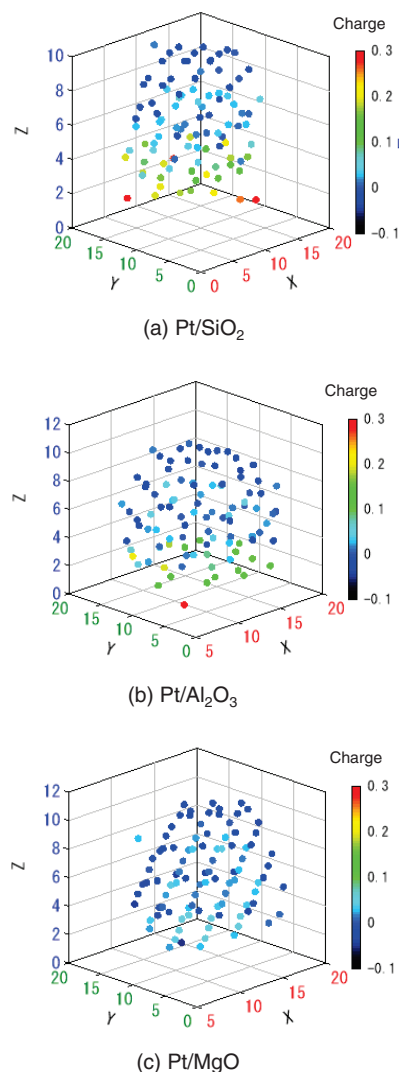


Fig. 8 Charge distribution of Pt cluster

acidity had correspondingly greater electron-withdrawing effect. This caused the platinum particles as a whole to have a greater positive charge, and the positive charge was concentrated in the vicinity of the interface.

4.3.2. Oxygen molecule adsorption on platinum according to the slab model

It can be seen from Fig. 8 that the state of the surface charge on the platinum cluster differs in the acidic support and basic support. With the acidic support, in particular, the upper part of the platinum cluster is negatively charged while the part close to the support is positively charged. It was inferred, therefore, that this difference in the charged state could be having an influence on oxygen adsorption characteristics. A platinum slab model was therefore created to recreate the upper part of the platinum cluster and the portion close to the support and the oxygen adsorption energy was compared in order to investigate the kind of influence that the surface charge state of the platinum cluster has on oxygen adsorption characteristics. A slab model with Pt₃₂ atoms as shown in Fig. 9(a) was created for this purpose.

Next, in order to control the charges state of the platinum surface in the slab model, additional charges were applied to the slab model to give it different levels from -3 to +3, as shown in Fig. 9(a). The ab-initio calculation was carried out using this model. The result, as shown in Table 9, was that the applied charges succeeded in changing the surface charge of the platinum slab model within a range from -0.240 to +0.212. In addition, it was confirmed that the charge states of the platinum atoms in the three platinum cluster models shown in Table 8, which ranged from -0.05 to +0.32, were generally reproduced. This suggests that the surface states of the upper part of the platinum cluster and of the portion close to the support were simulated successfully.

4.3.3. Calculation of characteristics of oxygen adsorption on platinum in the slab model

The next step was to ascertain the influence that the electron state on the platinum surface has on oxygen

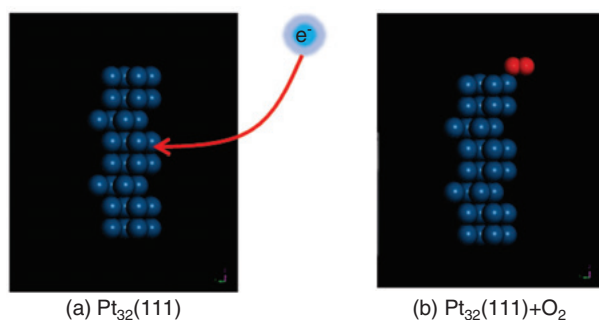


Fig. 9 Pt slab model and Pt+O₂ slab model

Table 9 Charge level of Pt surface

Total charge amount	-3	-1	0	1	3
Charge level of surface Pt atom	-0.240	-0.093	-0.017	+0.060	+0.212

adsorption characteristics. For this purpose, a model was created that has O₂ molecules adsorbed on the surface of the slab model shown in Fig. 9(a). Figure 9(b) shows a schematic illustration of this model. Ab-initio calculation of this model was carried out and Eq. (2) was then used to calculate the O₂ adsorption energy from the calculated energy before and after adsorption.



The results are shown in Fig. 10. The greater the charge applied, the larger ΔE_{ads} becomes. Where the charge was +3, the oxygen ends up being desorbed from the platinum surface following the stabilization calculation. In other words, this indicates that the greater the extent to which the platinum surface becomes positively charged, the more unstable the oxygen adsorption state will become, entering a state that tends to resist adsorption. From this it can be inferred that although a positive charge was concentrated on the platinum surface on the part of the platinum cluster close to the support in Fig. 8(a), the platinum surface of the part close to the support was in a state that tends to resist oxygen adsorption. This suggests, therefore, that the platinum surface close to the support on the platinum supported acidic support becomes a highly active site and promotes reaction.



Fig. 10 Oxygen adsorption energy on Pt surface

5. Discussion

When the results to this point are consolidated, they show, first of all, that the paraffin oxidation reaction of platinum supported catalyst using the SiO₂, Al₂O₃, and

MgO that were selected as model materials present the highest TOF and so the highest level of activity with the SiO₂. This confirms that the use of an acidic support yields higher paraffin oxidation performance. The analysis of material properties also shows that when the acidity of the support is higher, the electron state of the platinum particles will be in a metallic state. This shows that since oxygen adsorption is successfully inhibited, the use of an acidic support maintains the platinum in a state that tends to inhibit oxidation. It is further shown by ab-initio calculation that acidic support causes the platinum surface close to the support to become positively charged, and the oxygen adsorption state becomes unstable. This provides theoretical corroboration for the inhibition of oxygen adsorption.

Based on these results, the mechanism that promotes paraffin oxidation performance by means of the acidic support is as shown in Fig. 11. Since the acidic support withdraws electrons from the platinum particles, the platinum particles become electron deficient. This electron-withdrawing effect acts with particular effect on platinum atoms that are close to the acidic support, causing them to become positively charged, and the adsorption of oxygen consequently tends to be inhibited. The result of this is that the adsorption of paraffin is not blocked and paraffin oxidation reactions tend to proceed more readily. Therefore, the reaction mechanism that was inferred initially has been successfully corroborated by a combination of evaluation of activity, analysis of material properties, and theoretical computation.

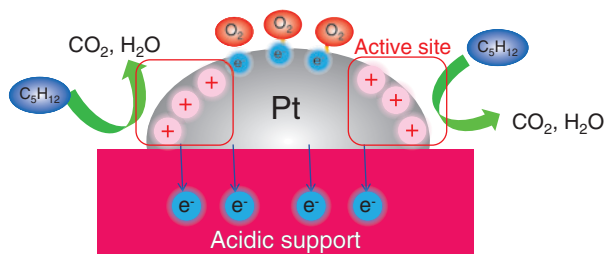


Fig. 11 Schematic image of HC oxidation on Pt supported catalyst

6. Conclusion

Platinum supported acidic support catalyst yields high performance as an HC purification catalyst for lean burn engines. The mechanism that causes that performance was elucidated by selecting SiO₂, Al₂O₃, and MgO as acidic, neutral, and basic model materials and subjecting them to evaluation of activity, analysis of material properties, and ab-initio calculation. The following was learned as a result:

- (1) The evaluation of activity showed that higher acidity in

the support results in correspondingly higher paraffin purification performance.

- (2) The analysis of material properties showed that when platinum particles are on an acidic support, they more readily retain a metallic state and oxygen adsorption on the platinum surface is inhibited.
- (3) The ab-initio calculation showed that platinum particles on an acidic support are positively charged and that the positive charge is particularly concentrated on the surface of platinum particles that are close to the support. It was also found that when the surface of a platinum particle is positively charged, it tends to resist the adsorption of oxygen.

These observations successfully corroborated that the cause of the high level of purification performance shown by platinum supported acidic support catalyst is the electron activity of the acidic support, which inhibits oxygen adsorption on the surface of platinum that is close to the support, and that this produces the high level of activity.

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