

Effects of Carbon Number and Bond Saturation on Hydrocarbon Combustion over Diesel Oxidation Catalyst

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One of the problems in a diesel oxidation catalyst is insufficient activity for injected diesel fuel at low temperatures caused by strong adsorption of hydrocarbons. This study systematically clarified the poisoning effect of various hydrocarbons having carbon number from 3 to 16. As carbon number in alkane increased, the light-off temperature over a Pt-Pd/Al₂O₃ catalyst gradually shifted to lower temperature. While alkenes and aromatics showed opposite trend; the light-off shifted to higher temperature as carbon number increased. In-situ FTIR spectra indicated that the amount of adsorbed hydrocarbon on metal surface increased with the increase in carbon number of alkanes and alkenes. Kinetic analysis showed that the reaction orders with respect to O₂ were below zero in light alkane combustion, while those with respect to hydrocarbons were zero or lower in alkene and aromatic combustion. The shift of the light-off temperature was rationalized by competitive adsorption of hydrocarbons and oxygen.

Introduction

In clean diesel vehicles, particulate matter (PM) from an engine is trapped in a ceramic filter (Diesel Particulate Filter, DPF), and then accumulated particulate is continuously or periodically burned off. A Pt-Pd-based diesel oxidation catalyst (DOC) converter is placed upstream of DPF, which plays an important role for PM removal.^{1,2} Since the diesel exhaust temperature is usually 200 – 300 °C,³ DOC supplies NO₂ as a strong oxidant for PM combustion by oxidation of NO with O₂ during continuous regeneration. For entire regeneration of DPF, the exhaust temperature is increased to 600 °C by combustion of excess fuels injected into DOC. For a better fuel economy, effective combustion of injected fuels in DOC is required. However, at lower exhaust temperatures, the hydrocarbon combustion insufficiently proceeds because of strong adsorption of unburned components in fuels on active sites of DOC.

Diesel fuel contains various types of hydrocarbons (HC): *n*-alkanes such as *n*-cetane, iso-alkanes such as iso-cetane and 2-methylpentadecane, cyclo-alkanes such as *n*-dodecylcyclohexane and decalin, and aromatics such as 1-methylnaphthalene.⁴ The carbon number in the diesel fuel components are widely distributed from 8 to 20. In order to design better catalysts and optimum operation of DOC, systematic understanding is necessary for the poisoning effect and interaction of these wide range of components in fuels with noble metal surfaces. In the research area of hydrocarbon

oxidation over noble metal catalysts, several papers have been published focusing on specific components. It is well reported that light alkenes, such as propene, cause poisoning effect on noble metal catalysts during so called “cold-start”.⁵⁻⁹ Tanabe et al. investigated propene oxidation on Pt/Al₂O₃ by means of operando-XAFS, and clarified preferential adsorption of propene on both metallic and oxidized Pt below 160 °C, which cause self-poisoning effect.^{5,6} Hermann et al. reported propene induced reversible deactivation of Pt/Pd-based oxidation catalyst.⁹ They demonstrated the deactivation of oxidation activity in the second and third run due to strong adsorption of propene. Due to difficulty in experimental research using heavy hydrocarbons, the research on the poisoning effect by higher hydrocarbons is still limited. Uchisawa et al. clarified that heavy hydrocarbons are injected to DOC as a mixture of vapor and liquid droplet due to their high boiling point, and the liquid droplet sometimes cause pore-blocking which suppress the diffusion of hydrocarbons to active metal surfaces.¹⁰⁻¹²

Some of the papers reported systematic investigations on the combustion of diesel fuel components. Yao et al. correlated the combustion activity of linear alkanes with ionization energy, which means that the C-H bond cleavage is the rate-limiting step for combustion of higher alkanes as well as lower alkanes.¹³ Diehl et al. clarified the flammability of heavy hydrocarbons having carbon number from 6 to 20 as follows:¹⁴ (1) Linear alkanes improve combustibility with the increase in the number of carbon atoms, (2) branched alkanes are less flammable than straight chain alkanes having the same carbon number, (3) there is little effect of carbon number on linear alkene oxidation, (4) branched and cyclic alkenes are more combustible than alkenes with the same carbon number, (5) monocyclic aromatics are less combustible with alkyl

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substituents, and (6) polycyclic aromatics are less flammable than cyclic alkanes with the same carbon number.

The flammability of hydrocarbons is the critical factor for the catalytic combustion; however, this is not a sole factor. Since catalytic combustion is affected by the adsorption of both hydrocarbon and oxygen, the competitive adsorption of oxygen on the catalyst surface should be considered. The purpose of this study is to clarify the poisoning effect of various hydrocarbons in diesel fuels, using wide range of carbon numbers and various types of hydrocarbons, aiming a better design of DOC systems and appropriate injection of fuels. The state of adsorbed hydrocarbons was observed by in-situ FTIR, and the strength of competitive adsorption of hydrocarbons and oxygen was estimated by kinetic analysis.

Experimental

Catalyst preparation

A model diesel oxidation catalyst, Pt-Pd/Al₂O₃, was supplied by the project of Automotive Internal Combustion Engines (AICE). Pt-Pd/SiO₂ was prepared by impregnating aqueous solutions of Pt(NO₃)₂ and Pd(NO₃)₂ to SiO₂ (Reference catalyst from Catalysis Society of Japan, JRC-SIO-5), followed by an evaporation and dryness. For both Pt-Pd/Al₂O₃ and Pt-Pd/SiO₂, the contents of Pt and Pd were 1.73 wt% and 0.86 wt%, respectively. The catalysts were aged in air at 700 °C for 30 h. The dispersions of supported metals and surface areas are 5.3 % and 136 m² g⁻¹ for Pt-Pd/Al₂O₃, and 4.6 % and 166 m² g⁻¹ for Pt-Pd/SiO₂, respectively.

Catalytic tests

The catalytic tests of HC combustion were carried out in a fixed bed flow reactor at atmospheric pressure. Various *n*-alkane, 1-alkene having carbon numbers from 3 to 16 were used as substrates. For aromatic compounds, toluene and 1-methyl naphthalene were examined. The compositions of feed gas were 2000 ppmC HC, 10% O₂, and Ar as a balance, and the mixture gas was flown to a 100 mg catalyst at a rate of 600 mL min⁻¹ (GHSV = 360,000 mL g⁻¹h⁻¹). Propane and propene were supplied from gas cylinders. Other liquid hydrocarbons were supplied by passing Ar flow in a saturator keeping temperature from -42 to 115 °C to obtain required vapor pressure of HC. At first, a catalyst was pretreated in a flow of 10% O₂/Ar at 500 °C for 30 min, then the catalytic activity was measured at the catalyst bed temperature from 300 to 100 °C at a decrease rate of 5 °C min⁻¹. If the catalyst activity measured while raising the temperature, the adsorbed species at lower temperature may remained on the catalyst surface and affect the measurement on the next higher temperature. Therefore, the catalyst activity was measured while lowering the temperature. The effluent gas was analyzed by Horiba VA-3112 and VS-3003 dual-beam non-dispersive infrared absorption CO/CO₂ analyzer. Kinetic parameters were estimated by varying the HC concentrations in the range from 1000 to 8000 ppmC, and the O₂ concentrations in the range from 4 to 13%. The kinetic analyses were conducted at a temperature where the conversion of each hydrocarbon was 30%.

Characterization of catalysts

In-situ FTIR spectra of adsorbed species were obtained using JASCO FT/IR-6100 equipped with an in-situ diffuse reflectance unit (JASCO DR-650Ai) under the same conditions to the catalytic tests by the flow apparatus. Metal dispersion was estimated by CO adsorption using Microtrac-Bel Belcat-B. BET surface area was measured by Microtrac-Bel Belsorp Mini II.

Results and Discussion

Light-off temperature - Dependence on HC type and carbon number

Figs. 1–3 show the temperature dependence of CO₂ production in the oxidation of *n*-alkanes, 1-alkenes, and aromatics over Pt-Pd/Al₂O₃ catalyst. It should be noted that the production of CO was negligible. For *n*-alkanes, the light-off shifted to lower temperature with the increase in carbon number, i.e., the light-off temperature of propane (C₃) was 180 °C, while that of cetane (C₁₆) decreased to 100 °C (Fig. 1). This result agrees well with the report by Diehl et al.,¹⁴ which showed shift of the light-off of *n*-alkanes to lower temperatures as the carbon number in HC increased from *n*-hexane (C₆H₁₄) to *n*-eicosane (*n*-C₂₀H₄₂). For 1-alkenes in contrast, the light-off shifted to higher temperature as the carbon number increased from propene to octene, and slightly shifted above octene (Fig. 2). For aromatics, the trend was similar to that of 1-alkenes, i.e., the combustion temperature of toluene was lower than that of 1-methylnaphthalene (1-MN) (Fig. 3). As an indicator for the reactivity of HC, the temperature at which the HC conversion reached to 30% was defined as T₃₀. As shown in Fig. 4, T₃₀ of *n*-alkanes decreased with the carbon number, while those of 1-alkenes and aromatics increased. In other words, heavy alkanes and light alkenes and aromatics showed higher reactivity.

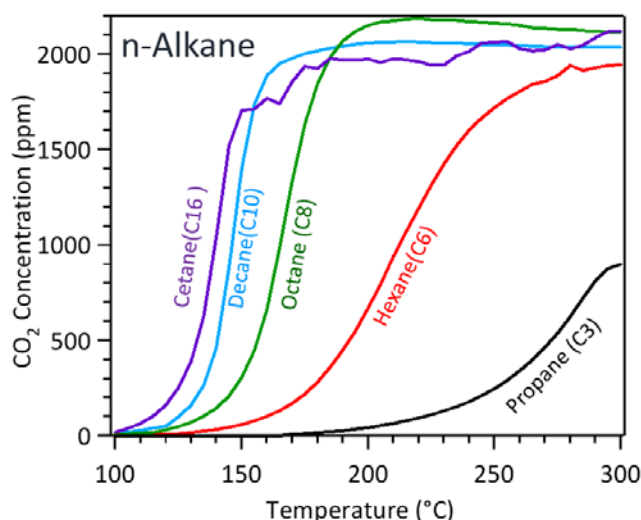


Fig. 1. Temperature ramp for combustion of *n*-alkanes.

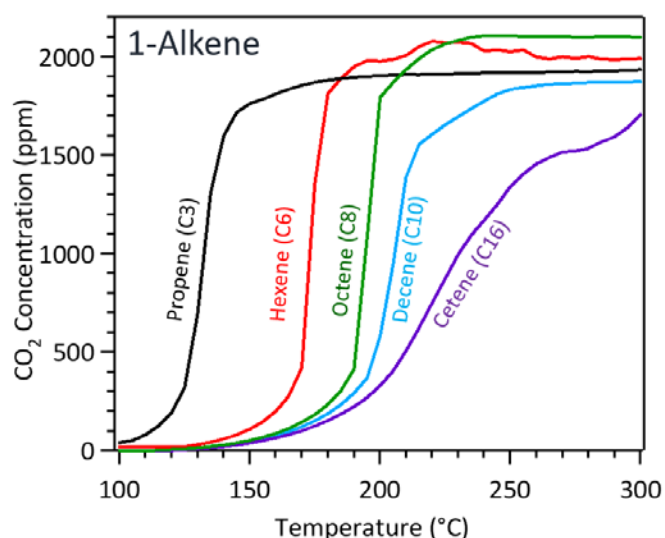


Fig. 2. Temperature ramp for combustion of 1-alkenes.

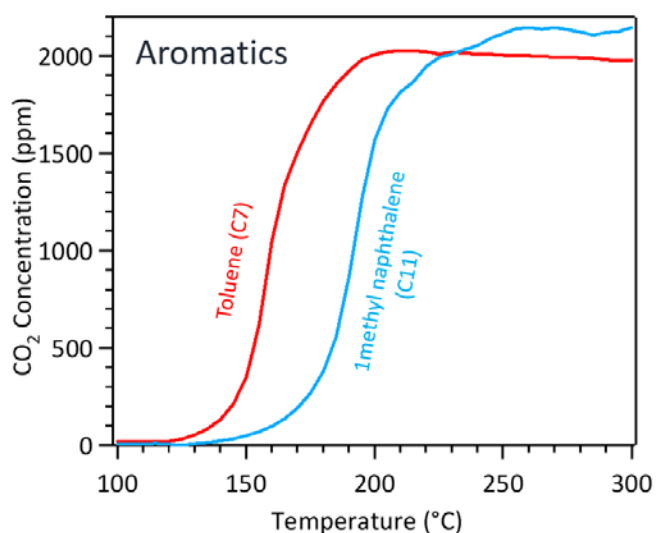
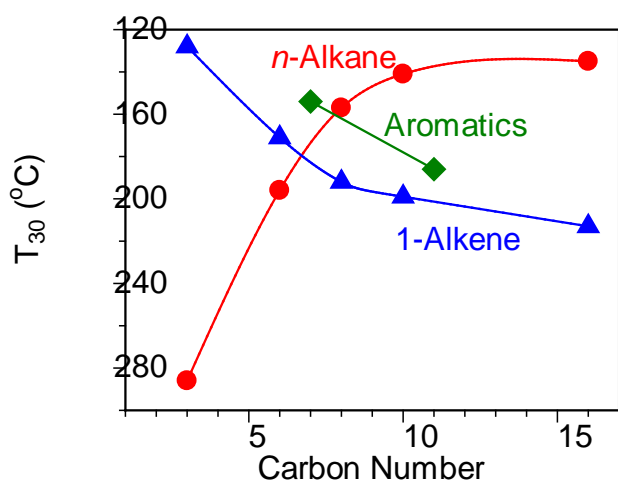


Fig. 3. Temperature ramp for combustion of aromatics.

Fig. 4. Dependence of T_{30} on carbon number in *n*-alkanes, 1-alkenes, and aromatics.

Generally, the catalytic reactivity of HC can be explained by (1) flammability of HC, (2) poisoning by HC adsorption, (3) poisoning by coke formation, and (4) sintering of metal particles on catalysts. It should be noted that the activity patterns were reproducible for several catalytic runs. Therefore, irreversible changes in the catalysts, i.e., (3) poisoning by coke formation and (4) sintering of metal particles, can be ruled out in this study. The reactivity of hydrocarbons can be expressed by the C-H and C-C bond strength because the fission of these bonds is related to rate determining step of HC oxidation.^{13,15} Since the bond strength generally decreases with the carbon number increases, the trend in 1-alkenes cannot be explained. Therefore, self-poisoning is the most possible explanation of the trend in Fig. 4. Actually, it is reported that propene strongly adsorbs on Pt surface, causing self-poisoning of catalysts.^{5,6} In order to directly observe the effect of adsorption of HC and its derivatives, FTIR spectra of adsorbed species on catalysts were measured under the reaction conditions.

In-situ FTIR spectra of adsorbed species under the reaction conditions

Fig. 5 shows in-situ FTIR spectra of adsorbed species on Pt-Pd/Al₂O₃ under the combustion of various HC at 250 °C. For all the spectra, wide and complicated absorption bands were observed in the range from 1400 to 1700 cm⁻¹. The broad bands can be assigned to the CO stretching mode of carboxyl groups,^{16,17} such as acetate and formate, and ring vibration mode of benzene and naphthalene.^{18–20} Interestingly, as increase in the intensity of the bands at 1400–1700cm⁻¹, a negative band at 3750 cm⁻¹ was enhanced. The band at 3750 cm⁻¹ is attributed to hydroxyl groups on Al₂O₃.^{21,22} The negative correspondence of these bands indicates the adsorption of carboxylates or aromatics on -OH species on Al₂O₃. The adsorption of oxygenated hydrocarbons of Al₂O₃ was also reported by O'Brien et al.¹⁷ They carried out temperature programmed oxidation of Pt/Al₂O₃ after propane combustion, and observed CO₂ formation peak at 300–600 °C assignable to surface enolate, ester, acetone, and acetate.¹⁷ The intensity of the broad bands assignable to C=O stretching mode at 1400–1700 cm⁻¹ was almost the same irrespective of carbon number and bond saturation of HC. From the FTIR spectra, it can be depicted that hydrocarbons are partially oxidized to form surface carboxylates, such as acetate and formate. By detection of CO₂ during O₂ treatment of the spent catalyst at 500 °C, the amount of carbon in adsorbed carboxylates on the catalyst was at 5.3–6.8 × 10⁻⁶ mol m⁻². It is reported that the surface concentration of cation sites on (110) plane of γ-Al₂O₃ is 9.8 × 10⁻⁶ mol m⁻².^{23,24} When alumina surface is fully covered with acetate and formate by forming bidentate or monodentate species, the amount of adsorbed carbons can be estimated as 2.5–9.8 × 10⁻⁶ mol m⁻². Since the value is close to the amount of obtained CO₂, the surface sites on alumina support are almost saturated with partially oxidized hydrocarbons. The exposure of noble metal atoms was estimated at 0.16 × 10⁻⁶ mol m⁻² by CO adsorption. The far higher number of carboxylates than the exposed noble metals

indicates that most of the carboxylates should migrate to Al_2O_3 support surface, and strongly adsorbed on Al_2O_3 by substitution with basic OH groups. Since the adsorbed carboxylates are present on the support surface in most part, and their amount was independent of the types of aliphatic hydrocarbons, the ignition temperature dependence on carbon number and bond saturation in HC cannot be rationalized by poisoning effect of the surface carboxylates.

In Fig. 5, another small wide band was observed at 2950 cm^{-1} for aliphatic HC and at 3100 cm^{-1} for aromatics which can be assigned to C-H stretching mode. The bands became stronger as increase in the carbon number, and alkenes and aromatics showed higher intensity than that of alkanes. There are two possibilities for the chemical species giving the C-H stretching band, i.e., one is unreacted hydrocarbons and the other is oxygenated hydrocarbons on Al_2O_3 support. To eliminate the contribution of latter species, the FTIR measurements were carried out by using Pt-Pd/ SiO_2 catalyst, because SiO_2 is known as a chemically inert support. Due to absence of basic sites on SiO_2 , surface oxygenated hydrocarbons hardly adsorb on SiO_2 .

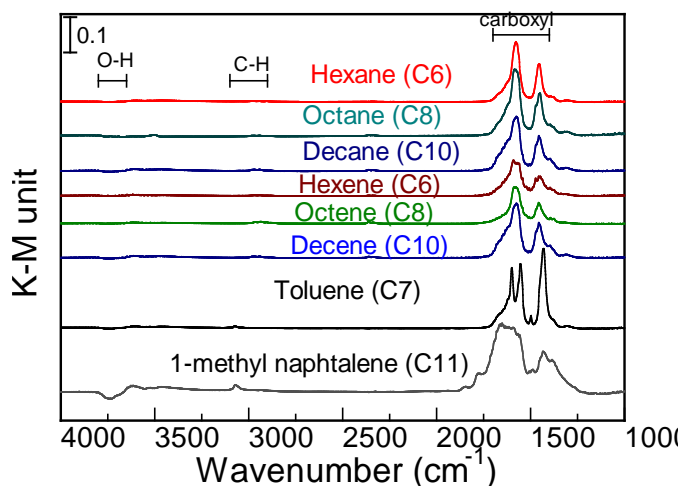


Fig. 5. In-situ FTIR spectra of adsorbed species on Pt-Pd/ Al_2O_3 under the reaction conditions of HC combustion at $250\text{ }^\circ\text{C}$.

Fig. 6 shows in-situ FTIR spectra of adsorbed species under aliphatic hydrocarbon combustion over Pt-Pd/ SiO_2 . The adsorption temperature was $150\text{ }^\circ\text{C}$ to avoid partial oxidation of HC to oxygenates. Because of too high boiling point ($240\text{ }^\circ\text{C}$) of 1-methylnaphthalene, the FTIR spectra of aromatic compounds cannot be compared without partial oxidation. In the case of decene, the band assignable to surface carboxylates were observed in the range of $1400\text{--}1700\text{ cm}^{-1}$ together with bands of CO_2 around 2350 cm^{-1} . These bands indicate that a part of decene was oxidized to carboxylates and CO_2 . On the other HC, the formation of surface oxygenates was fairly suppressed. Clearly, all the spectra of adsorbed aliphatic hydrocarbons showed C-H stretching mode of HC at 2950 cm^{-1} . The negligible change around 3750 cm^{-1} (hydroxy groups of SiO_2 support) indicates negligible adsorption of HC on SiO_2 support and selective adsorption on noble metals. The

adsorbed alkenes showed higher C-H band intensity than that of alkanes. This is due to the strong interaction of π -orbital in C=C bond with coordinatively unsaturated sites of noble metal surface, followed by the formation of di- σ bond between alkenes and noble metal surface.^{25,26} Irrespective of C-C bond saturation, the C-H stretching band became stronger with the increase in the carbon number of HC. Although the adsorption of aromatics on noble metal surface was not experimentally compared, the strong adsorption of aromatics on noble metal surface is well known. Actually, the heat of adsorption of benzene on Pt(111) was -244 kJ mol^{-1} as estimated by Carey et al. using calorimetry.²⁷ Morin et al. compared the adsorption of polycyclic aromatic hydrocarbons on Pt(111) surfaces by periodic density functional theory calculations, and clarified the increase in adsorption energies per molecule as in the order of benzene < naphthalene < anthracene.²⁸ Therefore, with the increase in carbon number, the interaction with noble metal surface increases for alkanes, alkenes, and aromatics. The shift of T_{30} of alkenes and aromatics to higher temperature can be rationalized by stronger adsorption of heavy HC on noble metal surface. However, the shift of T_{30} of *n*-alkanes to lower temperature cannot be explained by adsorption strength of HC on noble metals. Then, the contribution of O_2 adsorption was also examined by kinetic analyses.

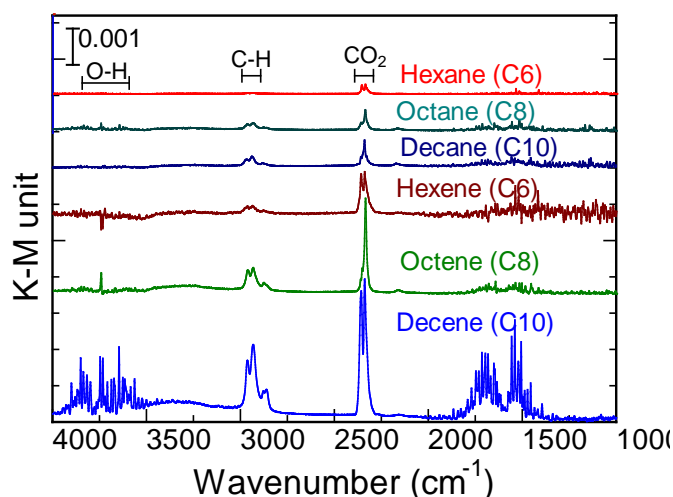


Fig. 6. In-situ FTIR spectra of adsorbed species on Pt-Pd/ SiO_2 under the reaction conditions of HC combustion at $150\text{ }^\circ\text{C}$.

Reaction order with respect to HC and O_2

For quantitative evaluation of the effects of adsorption of both HC and O_2 , the kinetic analysis was carried out and the reaction orders with respect to HC and O_2 concentrations were estimated. Generally, the order of the reaction would be 0.5–1.0 when a reaction proceeds with Langmuir-Hinshelwood mechanism, while that would be around 0 when the substrates are saturated on catalyst surface. Furthermore, when a substrate also acts as an inhibitor, the order of the reaction would be negative value (so-called self-poisoning). Typical example is CO oxidation over noble metal catalysts. Berlowitz et al. performed kinetic analysis of CO oxidation on Ir (111)

surface, and demonstrated that the reaction order with respect to CO is 1 when CO concentration (denoted as [CO], hereafter) is in the range from 0.1 to 1 torr, while that becomes -1 when [CO] is in the range from 5 to 50 torr.²⁹ The negative order at the higher CO concentration indicates the inhibition of the dissociative adsorption of O₂ by strongly adsorbed CO on Ir surface.

The typical results of the dependence of CO₂ formation rates on HC and O₂ concentrations (denoted as [HC] and [O₂], hereafter) are shown in Figs. 7 and 8. The reaction order with respect to [O₂] can be determined based on the following equations.

$$\text{Rate} = k [\text{HC}]^m [\text{O}_2]^n \quad (\text{eq1}).$$

$$\ln(\text{Rate}) = \ln k + m \ln[\text{HC}] + n \ln[\text{O}_2] \quad (\text{eq2}).$$

When [HC] is constant, $\ln k$ and $m \ln[\text{HC}]$ are constant values, so that we can determine the order n from the slope of the logarithmic charts. In the case of decane, the CO₂ formation rate monotonously decreased with the concentration of O₂, indicating negative reaction order with respect to O₂ (Fig. 7). On the other hand, the CO₂ formation rate monotonously increased with the concentration of decane in the range from $\ln[\text{decane}] = 6.9$ to 8.3 (1000 to 4000 ppm). The slope of the plot became around zero above $\ln[\text{decane}] = 8.3$, indicating saturation of catalyst surface with adsorbed decane.

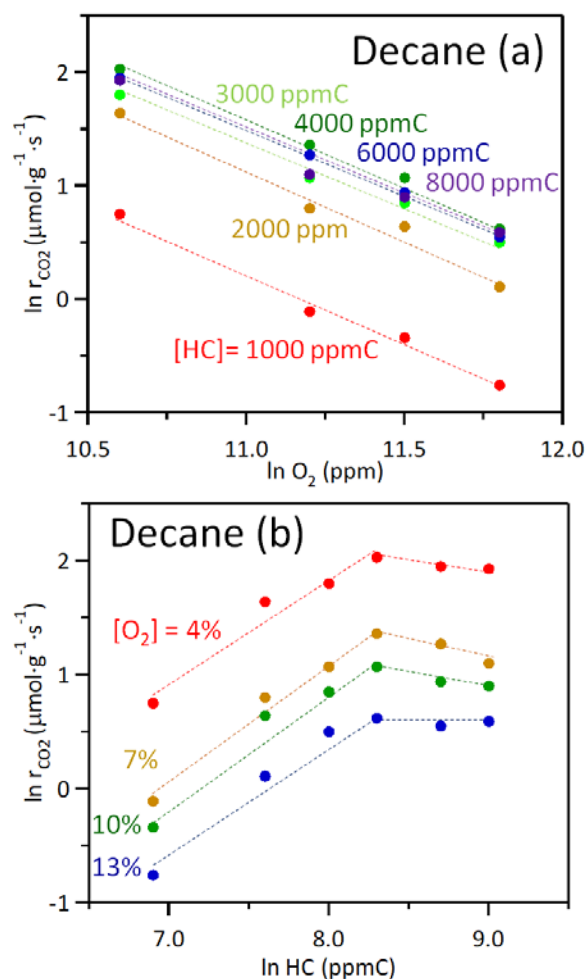


Fig. 7. Logarithmic charts of the dependence of CO₂ formation rate on (a) O₂ and (b) *n*-decane at 160 °C.

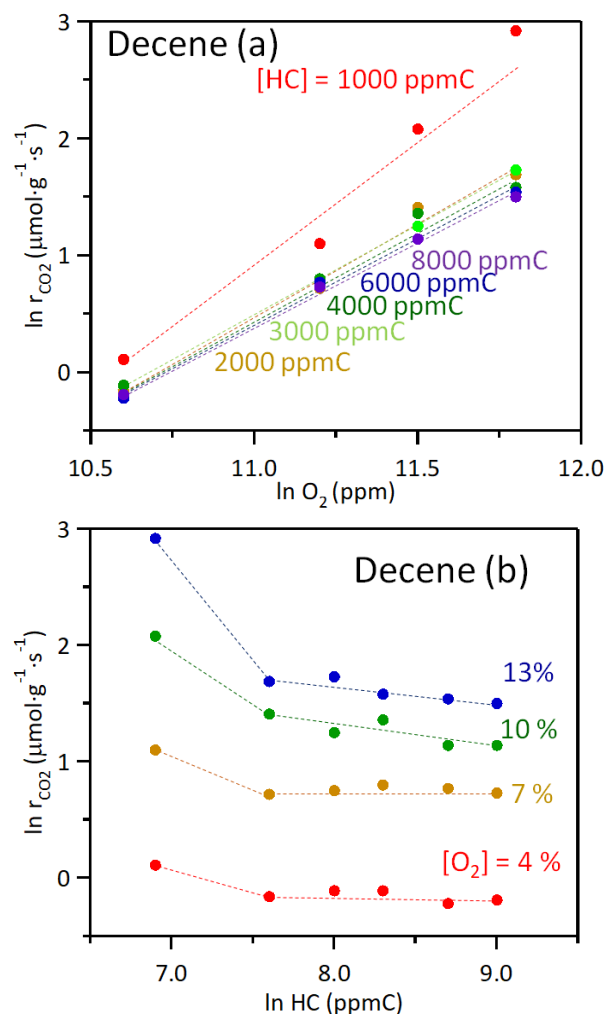


Fig. 8. Logarithmic charts of the dependence of CO₂ formation rate on (a) O₂ and (b) 1-decene at 230 °C

Since the effects of carbon number and bond saturation on T_{30} are compared at [HC] = 2000 ppmC and [O₂] = 7% in Fig. 4, the reaction orders were determined at these conditions and summarized in Table 1. In the combustion of alkanes, the reaction orders with respect to [HC] are around 1, while those with respect to [O₂] are negative value. The results indicate the stronger adsorption of O₂ than alkanes, in other words, the adsorption of light alkanes is weak for competitive adsorption with O₂. When cetane (C₁₆) is used as reductant, the reaction orders with respect to [O₂] and [cetane] are almost the same, suggesting comparable adsorption strength of cetane and O₂. The trend is in harmony with the in-situ FTIR results which showed the larger adsorption of heavier HC on noble metal surface. In the combustion of alkenes, the trend was opposite to alkanes (Fig. 8). The reaction order with respect to [O₂] is around 1, while those with respect to [HC] are zero or slightly negative value. Yao et al. also reported that

the reaction orders of the propene oxidation on supported Pt catalyst were negative with respect to propene but positive with respect to O_2 .¹³ As demonstrated stronger adsorption of alkene than alkane by in-situ FTIR, it is reasonable that the orders with respect to [alkene] were lower than those of [alkane]. The effect of carbon number was small in alkene combustion. It can be speculated that the stronger adsorption on noble metal by C=C bond than by saturated C-C bonds weakened the effect of carbon number. The negative reaction orders with respect to [HC] for aromatics indicates strong adsorption of aromatics on noble metal surface. The results in Table 1 indicates that the effects of carbon number and bond saturation can be rationalized by strength of HC adsorption relative to O_2 .

Table 1. Reaction orders for HC combustion with respect to HC and O_2 concentrations. The standard concentrations of HC and O_2 were HC = 2000 ppmC and O_2 = 7%, respectively.

Type of HC	Carbon number	Reaction order to HC ^a	Reaction order to O_2 ^b	Temperature (°C)
Alkane	6	0.9	-0.6	210
	10	1.1	-1.2	160
	16	0.7	0.5	150
Alkene	6	-0.2	1.2	190
	10	0.0	1.5	230
	16	0.0	1.3	230
Aromatics	7(toluene)	-0.3	0.6	180
	11(1-MN)	-0.4	1.0	200

a) O_2 = 7%, b) HC = 2000ppmC.

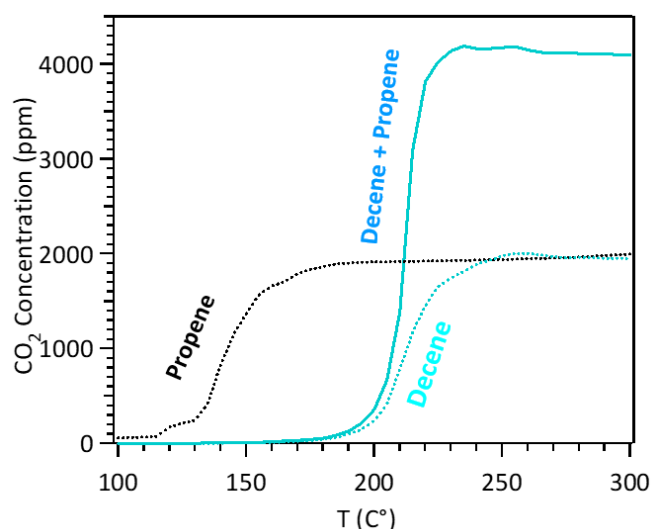


Fig. 9. Temperature ramp for combustion of propene, decene, and simultaneous combustion of propene and decene. The compositions of feed gas are 2000 ppmC propene, 2000 ppmC decene, 10% O_2 , and Ar as a balance.

Competitive oxidation of decene and propene

The above results demonstrated that the light-off temperature is affected by competitive adsorption of substrates. In order to confirm the effect of competitive adsorption, the oxidation reaction was examined using two hydrocarbons, decene and propene. As shown in Fig. 9, the light-off temperature of propene (110 °C) is lower than that of decene (170 °C), which can be rationalized by self-poisoning by stronger adsorption of decene. When these two hydrocarbons are simultaneously introduced to Pt-Pd/ Al_2O_3 catalyst, the formation of CO_2 started from 170 °C, which is the light-off temperature of decene. Propene was not oxidized below 170 °C under co-feeding of decene, though complete oxidation was observed at this temperature in simple propene- O_2 reaction. The result can be interpreted by the poisoning effect by decene, i.e., propene cannot be oxidized by blocking of catalyst surface by decene until strongly adsorbed decene was removed by desorption or oxidation.

Conclusions

The effects of carbon number and bond saturation in combustion of hydrocarbons over Pt-Pd/ Al_2O_3 catalyst were investigated on the basis of activity tests, in-situ FTIR spectra, and kinetic analysis. The ignition temperatures of hydrocarbons are controlled by the competitive adsorption of hydrocarbons and oxygen. The adsorption of oxygen is predominant in hexane and decane combustion, while cetane combustion proceeds in Langmuir-Hinshelwood type mechanism because of stronger adsorption on metal surface. Due to strong adsorption of 1-alkenes, the reaction order with respect to HC is nearly zero and that to O_2 is around 1. The orders of the reaction with respect to aromatic hydrocarbons are negative due to strong interaction with noble metals. The importance of adsorption strength of hydrocarbons relative to O_2 was clarified, which is worth for the design of diesel oxidation catalysts for complete oxidation of wide range of hydrocarbons.

Conflicts of interest

There are no conflicts to declare.

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