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Inhibition effect of carbon dioxide on the oxidation of hydrogen over a platinum foil catalyst

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Abstract

This paper investigates the catalytic ignition of the $H_2/O_2/CO_2$ mixture on platinum in a stagnation flow at atmospheric pressure experimentally and numerically. We measure the ignition temperatures of the gas mixtures flowing towards resistively heated platinum with various composition ratios and various diluent gases of N_2, Ar and CO_2. Compared with N_2 or Ar, the CO_2 dilution shows higher ignition temperature by about 50 K, even at the same composition ratio. The ignition temperature increase is proportional to the dilution ratio. Through the numerical simulation, it is illustrated that higher ignition temperature is caused by the adsorption of CO_2 and following dissociation on platinum surface, which was to date considered negligible in catalytic combustion.

Keywords: Hydrogen; CO_2 adsorption; Platinum; Catalytic; Ignition

1. Introduction

The combustion systems that use the oxygen and recycled flue gas mixture as oxidant have many benefits in the environmental point of view [1–3]. The combustion mixture used in this kind of systems contains no nitrogen, thus, emits no NO_x. Furthermore, carbon dioxide, a typical green house gas, can be easily collected from the combustor exit since the exhaust gas contains carbon dioxide with high concentration. In the dry recycle mode of the systems, where the flue gases are recycled after water removal, the oxidant can be regarded as the mixture of oxygen and carbon dioxide. The disadvantages of such systems are the complexity of the equipment and the significant reduction in efficiency caused by the need of pure oxygen [3]. Applying the catalytic combustion would be one of the solutions that compensate for the reduction of efficiency of the system because catalytic combustion as well known offers the potential for improved thermal efficiency. To apply catalytic combustion to such systems that use the recycled flue gas and oxygen as oxidant, it is a pre-requisite to understand the catalytic reaction of combustion mixture containing carbon dioxide.

Much literature has reported the characteristics of combustion mixture over platinum catalyst with nitrogen dilution postulating air as oxidant [4–8]. But, to the authors' knowledge, there is no research work about the combustion mixture with CO_2 as diluent gas.

Literature concerning CO_2 adsorption on platinum proclaims that the adsorption of CO_2 on platinum is

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negligible at room temperature or above [9–11]. van Tol et al. [11] mentioned that CO_2 is only weakly adsorbed on platinum at 80 K with an estimated heat of adsorption of at most 25 kJ/mol. They observed no CO_2 adsorption on the platinum surface at 90 K or above. Liu et al. [9] reported that no CO_2 adsorb on clean or oxygen-predosed Pt(1 1 1) at 112 K and estimated the heat of adsorption as about 40 kJ/mol.

But, most of the works were limited in high vacuum condition because the measurements are electron-based techniques. Due to the small mean free paths of electrons in gases at modest pressure, these studies are necessarily confined to model systems [12]. Therefore, there is always a doubt to extend their results to the case under atmospheric or high pressure.

As will be shown in this study, the CO_2 adsorption has a significant effect on the surface reaction over platinum at atmospheric pressure. We measure the heterogeneous ignition temperatures of $H_2/O_2/CO_2$ mixture over the platinum foil to reveal the effect of CO_2 on the catalytic reaction. Even if hydrogen does not produce CO_2, the investigation on the $H_2/O_2/CO_2$ mixture is crucial in the CO_2-recirculation system because the H_2 oxidation is a subset of the oxidation of hydrocarbon fuels. And, since hydrogen is frequently used to enhance or stabilize the burning of hydrocarbon, it is important to clarify the effect of CO_2 dilution on H_2 oxidation.

Through the numerical approach, we propose a model to predict the ignition temperature increase in the $H_2/O_2/CO_2$ mixture and find the mechanism which is responsible for the inhibition effect of CO_2 on platinum surface.

2. Experimental

The experimental apparatus is shown in Fig. 1. The platinum foil (99.95% purity, 2 mm × 25 mm, thickness: 0.025 mm) is installed in the cross-stream orientation in the reactor which has the square cross-section of 40 mm × 40 mm. The gas mixtures are introduced into the reactor with the uniform flow (8 cm/s) at room temperature and atmospheric pressure. The platinum foil is heated resistively. The temperature of the foil is controlled by the electric circuit designed to maintain a given temperature and is measured by the electric resistance since the resistivity of platinum is linearly proportional to temperature. In order to measure the resistance of the foil precisely, we use 4-wire method. The flow rate of the gas mixture is controlled by the MFC (Mass Flow Controller: BROOKS 5850E). The gases used in the experiments are prepared as pure gases (H_2, O_2, N_2, Ar: 99.999%; CO_2: 99.99%). CO concentration in the CO_2 gas is less than 4 ppm, which was measured by gas chromatography. Therefore, the error caused by CO impurities in CO_2 gas is negligible.

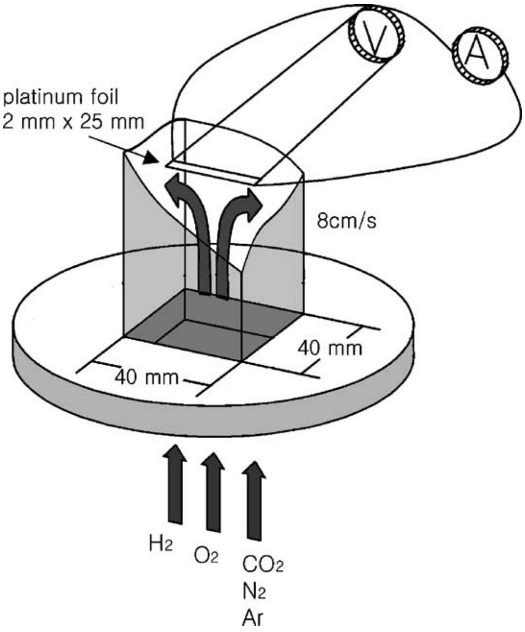

Fig. 1. Schematic diagram of experimental apparatus.

The temperature of the platinum foil is raised so that the foil reaches steady state. We define the ignition temperature as the temperature at which the power requirement begins to decrease (see Fig. 2).

Because the repetitive usage of the foil reduces the reactivity of platinum, we secured the reactivity of the specimen with the cleaning process proposed by Keck and Kasemo [13] before each experiment. The cleaning process is to let the 3.5% H_2/synthesis air mixture flow over the platinum foil at about 900 K for a few minutes.

Various combustion mixtures are examined. H_2 and O_2 are mixed with the fuel ratio ($H_2/(H_2 + O_2)$ by volume), which ranges from 20 to 65% and the H_2/O_2 mixtures are diluted with CO_2, N_2 or Ar, separately,

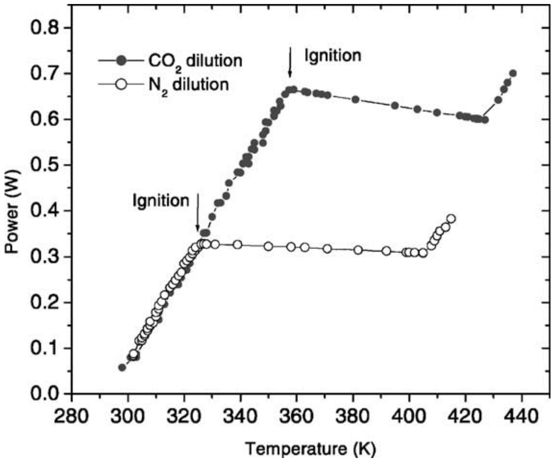

Fig. 2. Electrical power requirements for the platinum foil in combustion mixture flows (H_2:O_2:diluent gas = 0.02:0.08:0.90).

with the dilution ratio (diluent gas-to-mixture ratio by volume) ranging from 75 to 95%.

3. Numerical method

The numerical calculation is performed with SPIN [14] code which is one of the applications of the CHEMKIN Collection Release 3.6 software package. SPIN uses CHEMKIN [15], SURFACE CHEMKIN [16], and TRANSPORT [17], which defines the gas phase properties, the surface phase mechanism, and the transport properties, respectively. The numerical solver of SPIN [18] is the software that implements a Newton/time-step algorithm.

By SPIN, we can obtain the species distribution, velocity profiles and fluxes at the gas–surface interface as well as surface coverage. The surface temperature is determined by the energy balance at the interface: the conductive, convective, and diffusive energy transport in the gas phase are equilibrated with thermal radiation, chemical heat release and resistive heating on the surface [5]. The details of governing equations and solving strategies can be found in the manual of SPIN.

Actually, SPIN computes the stagnation flow field assuming infinite surface and infinitely extended gas inlet. But, by confining the attention to the center of the surface, edge effects coming from the finite dimension of the platinum foil can be neglected [5]. Also, the availability of the assumption has been proved in the previous similar works [5,19,20].

4. Chemical kinetics

In the present study, the gas phase reaction is not considered because, through the several calculations, we realized that the numerical results are not influenced by the gas phase reaction mechanism in the condition of our cases, i.e., lean mixtures and low temperatures.

The surface chemical mechanism is shown in Table 1. The elementary surface reactions of H_2 oxidation and CO oxidation (R1–R13 and R19–R23) were from Deutschmann et al. [6]. They validated their kinetic model with ignition temperature of H_2 and CO, respectively. The dissociation of the adsorbed CO_2 and reaction with other surface species (R15–R18) were proposed by Zerkle et al. [21]. They determined the activation energy of the reactions with thermodynamic constraints. The resulting surface energy level is consistent with well known gas-phase species enthalpies. The sticking coefficient of CO_2 (R14) is estimated with our experimental results. The site density used in this simulation is $1.63 \times 10^{15}\,\mathrm{cm}^{-2}$, which was estimated from the density of Pt [5].

5. Results and discussion

5.1. Experimental results

Fig. 2 shows the power requirements to retain the temperature of the foil when the fuel ratio is 20% and the dilution ratio is 90% (H_2:O_2:diluent gas = 0.02:0.08:0.90). The ignition temperature is defined, experimentally, by the temperature at which the power requirement begins to reduce even with increasing temperature. Decrease in power and increase in temperature is caused by the catalytic heating on the platinum surface. Because the power control is subjected to maintaining the temperature constant, the additional heat, from the catalytic surface reaction, compensates for the power requirement.

The ignition temperature of $H_2/O_2/CO_2$ mixture is higher than that of the combustion mixture with N_2 dilution, even at the same composition ratio. The

Table 1
Surface chemical kinetics

Reaction number[a]	Reaction	A[b] (cm mol s)	β	E (J/mol)
R1	$H_2 + 2Pt(S) \rightarrow 2H(S)$, FORD/Pt(S) 1.0/[c]	0.046	0.0	0.0, STICK[d]
R2	$2H(S) \rightarrow H_2 + 2Pt(S)$, COV/H(S) 0.0 0.0 −6000/[e]	3.7E+21	0.0	67400.0
R3	$H + Pt(S) \rightarrow H(S)$	1.00	0.0	0.0, STICK
R4	$O_2 + 2Pt(S) \rightarrow 2O(S)$	21.0	−1.0	0.0, STICK
R5	$2O(S) \rightarrow O_2 + 2Pt(S)$, COV/O(S) 0.0 0.0 −60000/	3.7E+21	0.0	213200.0
R6	$O + Pt(S) \rightarrow O(S)$	1.00	0.0	0.0, STICK
R7	$H_2O + Pt(S) \rightarrow H_2O(S)$	0.75	0.0	0.0, STICK
R8	$H_2O(S) \rightarrow H_2O + Pt(S)$	1.0E+13	0.0	40300.0
R9	$OH + Pt(S) \rightarrow OH(S)$	1.00	0.0	0.0, STICK
R10	$OH(S) \rightarrow OH + Pt(S)$	1.0E+13	0.0	192800.0
R11	$H(S) + O(S) \leftrightarrow OH(S) + Pt(S)$	3.7E+21	0.0	11500.0
R12	$H(S) + OH(S) \leftrightarrow H_2O(S) + Pt(S)$	3.7E+21	0.0	17400.0
R13	$OH(S) + OH(S) \leftrightarrow H_2O(S) + O(S)$	3.7E+21	0.0	48200.0
R14	$CO_2 + Pt(S) \rightarrow CO_2(S)$	0.022	0.0	0.0, STICK
R15	$CO_2(S) \rightarrow CO_2 + Pt(S)$	1.0E+11	0.0	27100.0
R16	$CO_2(S) + Pt(S) \rightarrow CO(S) + O(S)$, COV/O(S) 0.0 0.0 94000/	1.0E+11	0.0	173300.0
R17	$CO(S) + OH(S) \rightarrow CO_2(S) + H(S)$, COV/CO(S) 0.0 0.0 −33000/	5.4E+10	0.0	38700.0
R18	$CO_2(S) + H(S) \rightarrow CO(S) + OH(S)$	5.4E+10	0.0	28300.0
R19	$CO + Pt(S) \rightarrow CO(S)$, FORD/Pt(S) 2/	0.84	0.0	0.0, STICK
R20	$CO(S) \rightarrow CO + Pt(S)$	1.0E+13	0.0	125500.0
R21	$CO(S) + O(S) \rightarrow CO_2(S) + Pt(S)$	3.7E+21	0.0	105000.0
R22	$C(S) + O(S) \rightarrow CO(S) + Pt(S)$	3.7E+21	0.0	62800.0
R23	$CO(S) + Pt(S) \rightarrow C(S) + O(S)$	1.0E+18	0.0	184000.0

[a] R1–R13, R19–R23: [6]; R14: this work; R15–R18: [21].

[b] Rate expressions in the Arrhenius form, $k = AT^{\beta}\exp(-E/RT)$.

[c] FORD: the order for forward rate of progress is modified as indicated.

[d] STICK: sticking coefficient $\gamma = AT^{\beta}\exp(-E/RT)$, $k = \gamma/\Gamma^{m}\sqrt{RT/2\pi W}$, where Γ and W is total surface site concentration and molecular weight of the gas-phase species, respectively.

[e] COV/Z(S)$\eta\mu\varepsilon$/: rate expression modified by an activated coverage dependences as $k = AT^{\beta}\exp(-E/RT) \times (10^{\eta[Z]}[Z]^{\mu}\exp(\varepsilon[Z]/RT))$, where Z is the corresponding species.

$H_2/O_2/CO_2$ mixture requires more power, before ignition, than the N_2-diluted mixture.

Ignition temperature is a measure of catalytic reactivity of surfaces. Higher ignition temperature in the combustion mixture with CO_2, means that CO_2 has an inhibition effect on the H_2–O_2 reaction over the platinum surface. Comparing the power–temperature curves of the two mixtures, before ignition, the behavior is the same, which means that the differences in the heat transfer of gas flows are negligible. Therefore, the discrepancy between the mixtures cannot be explained with the diffusion characteristic in gas phase.

The ignition temperature variation of the combustion mixtures as a function of the fuel ratio, with the dilution ratio of 95%, is shown in Fig. 3. The ignition temperature of the N_2-diluted mixture can be compared with the results of Behrendt et al. [22]. The same trend and the similar range of the ignition tempera-

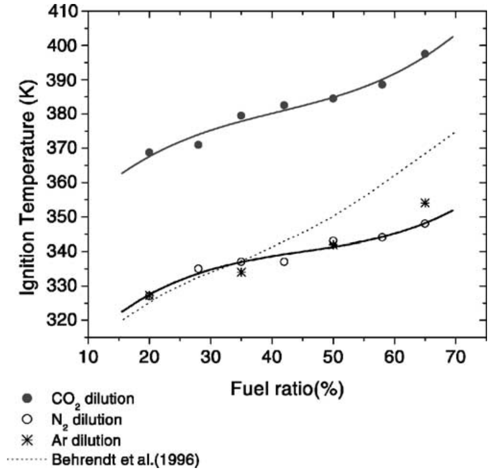

Fig. 3. Ignition temperature of the H_2/O_2 mixtures with various diluent gases at the dilution ratio of 95% (experiment).

tures prove that our results are reasonable. The little differences might be from several sources, such as the apparatus-dependency, the different dilution ratio of the mixtures, or the reactivity of the foil.

Nitrogen, as a diluent gas, shows the same behavior as argon which is known to be inert on catalyst surface. On the contrary, the $H_2/O_2/CO_2$ mixture ignites at higher temperature by about 50 K. The high ignition temperature of CO_2-diluted H_2/O_2 mixture implies that carbon dioxide has some effects on the catalytic combustion reaction.

The ignition process of the H_2 and O_2 mixture is explained as follows ([22], refer to Fig. 7). Before ignition, the platinum surface is covered with the hydrogen atom preventing oxygen from being adsorbed on the surface sites. As temperature rises, the desorption rate of hydrogen becomes higher than that of adsorption, thus, permitting oxygen to be adsorbed on the open sites. The adsorbed oxygen atoms react with hydrogen atoms forming OH radicals and water. The heat release from the oxidation reaction enhances desorption of hydrogen. This reaction cycle leads to ignition on the surface.

According to this theory, the ignition temperature of mixture increases with the increasing fuel ratio, because the high concentration of hydrogen in gas phase reinforces the adsorption of hydrogen on surface.

Fig. 4 shows the ignition characteristics with the given fuel ratios and the variation of dilution ratio. The ignition temperature increases with dilution ratio. Because the dilution reduces the partial pressure of reactants, H_2 and O_2, in gas phase, the surface reaction is more attenuated as the dilution ratio increase. Therefore, the ignition temperatures increase with dilution.

Since the CO_2 dilution has the direct effect of inhibition on the surface reaction as well as dilution effect in gas phase, the ignition temperature changes are more sensitive with increasing dilution ratio compared with the N_2 dilution. In other words, the difference in ignition temperature becomes larger as the dilution ratio increases.

Most probable explanation about the mechanism of the inhibition is that the adsorption of carbon dioxide and following surface reactions prevent the reactant, i.e., H_2 and O_2, from being adsorbed and reacting. Even though CO_2 adsorption strength is known to be weak over platinum, the large amount of CO_2 should be taken into account. Furthermore, since CO which is generated by the dissociation of CO_2 on platinum, is relatively more adsorptive, it is probable for CO to block the available surface site of platinum. Accordingly, the additional heat is required to remove CO and CO_2 from the surface in the case of the $H_2/O_2/CO_2$ mixture (see Fig. 2). The proof of the theory will be shown in the numerical results.

To verify the adsorption of CO_2 on the surface experimentally, we pre-exposed the foil to CO_2 gas in the same flow condition as the ignition experiment. That is, CO_2 was introduced in the reactor with the flow velocity of 8 cm/s, at atmospheric pressure for 1 min before the experiment. After the exposure, the ignition temperature of the $H_2/O_2/N_2$ mixture rises lightly as shown in Fig. 5. The result indicates that

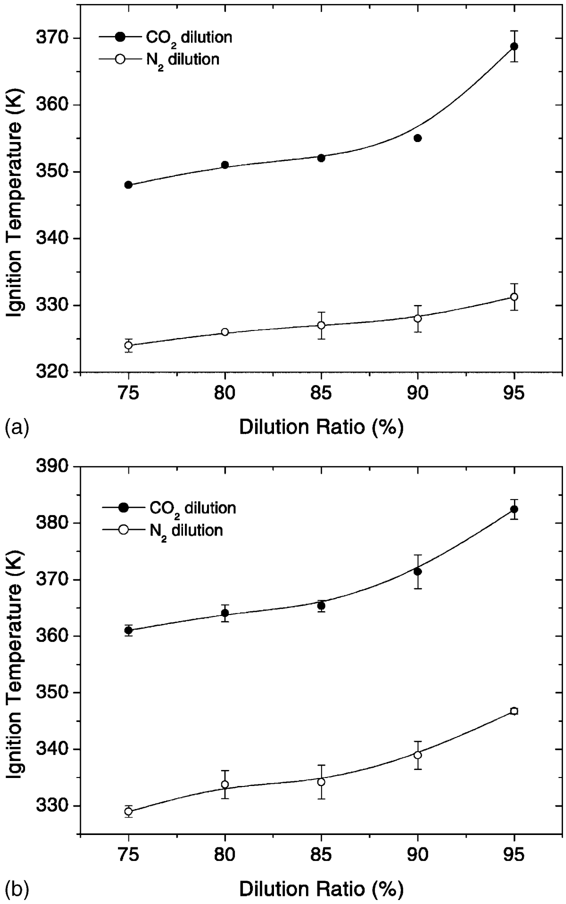

Fig. 4. Ignition temperature as a function of dilution ratio (experiment): (a) 20% fuel ratio and (b) 50% fuel ratio.

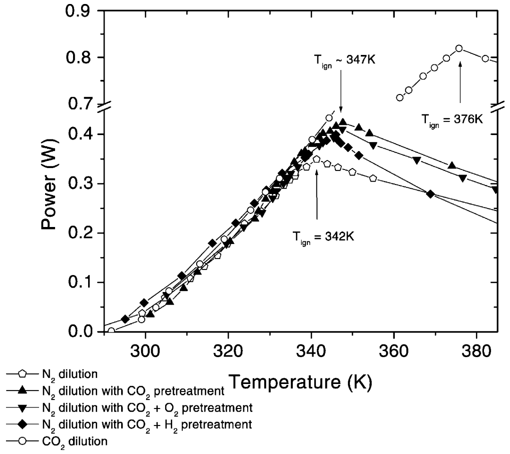

Fig. 5. Ignition temperature increases after the exposure for 1 min at 101,330 Pa (H_2:O_2:diluent gas = 0.05:0.05:0.90) (experiment).

the pre-adsorbed CO_2 inhibits the H_2–O_2 reaction on the surface. In the same way, H_2/CO_2 mixture (0.1/0.9 by volume) and O_2/CO_2 mixture (0.1/0.9 by volume) were employed for pre-treatment. Since the additional components, i.e., H_2 or O_2, of the pretreatment does not make change in the increment of the ignition temperature, we realized that neither H_2 nor O_2 promote the carbon dioxide adsorption on platinum.

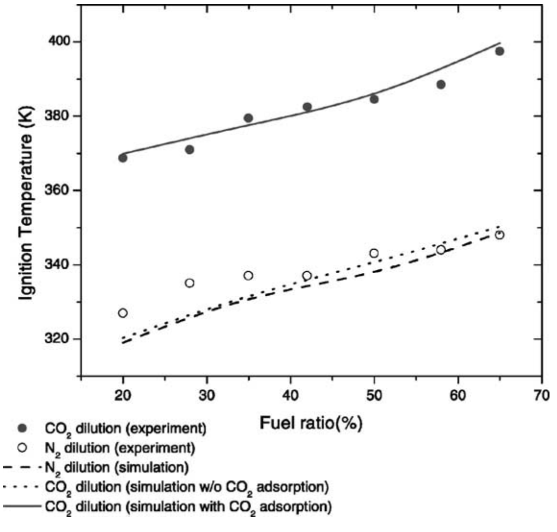

Fig. 6. Ignition temperature increases with the dilution ratio of 95%.

5.2. Numerical results

In the numerical calculation, the ignition can be defined with the rapid rise of the temperature without additional power input. The results are compared with the experimental results of the mixture of 95% dilution ratio in Fig. 6.

Without the adsorption reaction of CO_2 (R14), the ignition temperature of $H_2/O_2/CO_2$ mixture does not make any discrepancy with that of the $H_2/O_2/N_2$ mixture. This means that, as the power–temperature curves of experiments also show (see Fig. 2), the increment of ignition temperature cannot be explained with the feature of the mixture in gas phase.

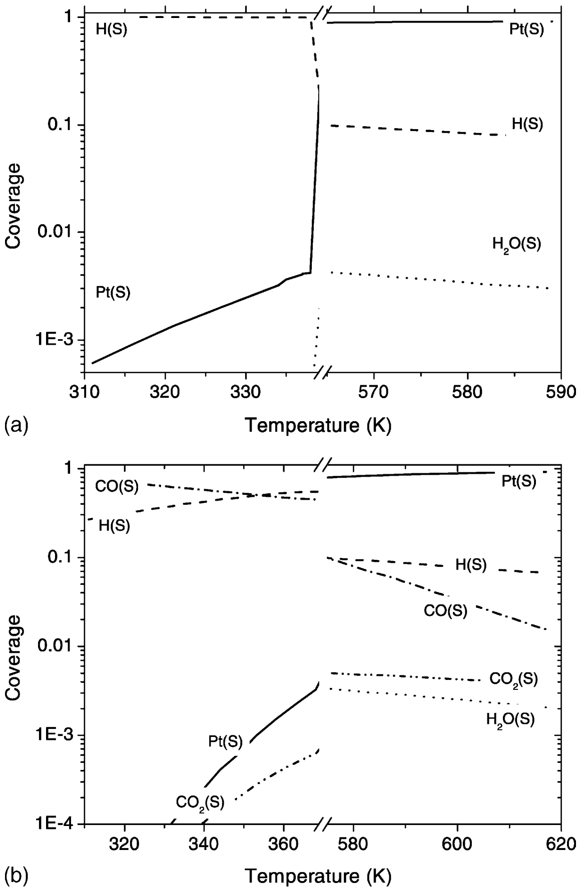

Fig. 7. Surface coverage before and after ignition of the mixtures at the same composition ratio (H_2:O_2:diluent gas = 0.025:0.025:0.95): (a) N_2 dilution and (b) CO_2 dilution.

When the adsorption of CO_2 (R14) and following reactions (R15–R23) are included in the surface reaction kinetics, we can successfully predict the ignition temperatures of the $H_2/O_2/CO_2$ mixtures. The estimated sticking coefficient is larger than 0.005 of Zerkle et al. [21]. Their estimation is based on the hydrocarbon fuel/air mixture in which CO_2 is produced only by fuel oxidation. But, in our case, due to large partial pressure of CO_2 in gas phase, CO_2 adsorption becomes more significant.

Fig. 7 illustrates the coverage change on the surface in terms of temperature at the composition ratio of H_2:O_2:diluent gas $= 0.025:0.025:0.95$. In the combustion mixture with N_2, before the ignition, hydrogen covers almost the whole surface sites. The ignition is initiated by desorption of the adsorbed hydrogen which allows oxygen to access the open sites and react (see Fig. 7(a)).

However, in the CO_2-diluted mixture, hydrogen shares the surface sites with CO which is originated from the adsorbed CO_2 (R16). In this case, desorption of hydrogen cannot initiate the reaction chain of ignition even at high temperature since CO inhibits oxygen from being adsorbed (see Figs. 7(b) and 8). Therefore, the ignition process does not proceed without desorption of adsorbed CO on the surface. The ignition occurs at the moment that CO leaves the surface sites considerably. In other words, the ignition temperature of the mixture is governed by the desorption characteristic of CO induced by CO_2 adsorption. After the ignition, CO and H leaves the surface rapidly and only small amount remains on the surface due to the high temperature of the surface (see Fig. 7(b)).

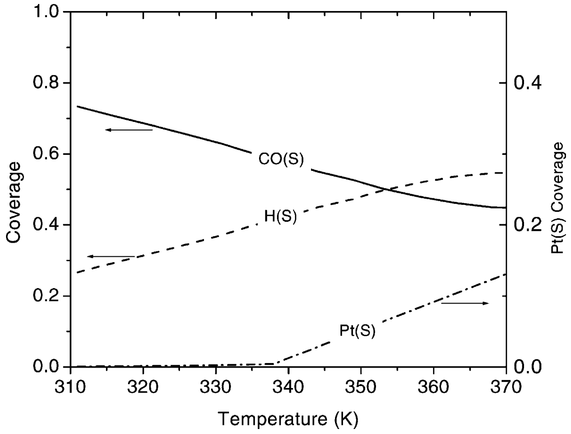

Fig. 8. Surface coverage before ignition of the $H_2/O_2/CO_2$ mixture (H_2:O_2:CO_2 $= 0.025:0.025:0.95$).

6. Summary and conclusion

To investigate the characteristics of combustion mixture with CO_2 dilution, we examined the heterogeneous ignition temperature of $H_2/O_2/CO_2$ mixtures on platinum at atmospheric pressure. The ignition temperature of CO_2-diluted mixture is higher than that of other dilution mixture, such as N_2 or Ar dilution by about 50 K. The difference in ignition temperature becomes larger as the mixture is diluted more.

Higher ignition temperature of CO_2-diluted combustion mixture is caused by inhibition effect of CO_2 on platinum surface. The numerical simulation shows that CO which is induced by CO_2 surface reaction prevents oxygen from being adsorbed and reacting with hydrogen on surface, and then increases the ignition temperature of combustion mixture. In order to understand the ignition delay in the $H_2/O_2/CO_2$ mixture on platinum, we should pay attention to CO_2 adsorption and dissociation on platinum.

Acknowledgements

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