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Reaction kinetics of H_2O adsorption on Ce surface

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Abstract

Cerium (Ce) thin films were prepared under an ultra high vacuum condition, and the reactivity of H_2O gas with the Ce surface was quantitatively measured for the reaction probability r_{H_2O} and the gas amount N_{H_2O} reacted at 298 K. The H_2O adsorption proceeded at the highest reaction rate even at 298 K on a clean Ce surface. As the H_2O reactivity drops, a marked desorption of H_2 gas from the surface was observed. From the measurement of the partial pressure of the desorbed H_2 gas, the reaction probability r_{2H/H_2O} of the H atoms from H_2O molecules were obtained. From the pressure dependence of the H_2O adsorption rate, the rate controlling step was estimated. The rate controlling step was found to be the dissociation of H_2O molecules on the Ce surface from the start to the end of the reaction. The activation energy for the H_2O adsorption was almost zero at $r_{H_2O}=1$, and then increased at $r_{H_2O}<1$. The activation energy for the surface reactions (hydride and/or hydroxide formations) of the H atoms from H_2O was almost zero at $r_{2H/H_2O}=1$, and then sharply increased at $r_{2H/H_2O}<1$ with increasing N_{H_2O}. The surface reactions of the H atoms from H_2O become strongly inhibited, and the recombination of the H atoms become active. Based on these data, complicated mechanisms of the H_2O adsorption on the Ce surface are discussed.
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1. Introduction

Ce is one of the interesting rare earth elements because of its high oxidation states and catalytic properties [1]. The easy transfer of O atoms between Ce_2O_3 and CeO_2 takes place by the ready change between the valence states Ce^{4+} and Ce^{3+}. This feature is utilized widely as a catalyst. Since misch metal (Mm) contains Ce (about 40 to 60 wt.%) as a main element, the catalytic features of Mm or Mm containing hydrogen absorbing alloys seems to be ascribed to the intrinsic catalytic feature of Ce. In a previous paper [2], we reported the quantitative reactivities, namely, reaction probabilities of H_2, O_2 or H_2O gas with the Ce surface at 298 K, and we elucidated that oxidized Ce surfaces exhibit much higher reactivities with H_2 than oxidized surfaces of other rare earths (La, Tb, Dy), however, the H_2O preadsorption layers on the Ce surface strongly reduce the H_2 reactivity. In addition, we found a fact that CeH_{2+x} hydrides exhibit higher reac-

tivities with O_2 than the Ce oxide surface, suggesting a high metallic property of CeH_{2+x} hydrides.

In this study we investigated the reaction mechanisms of H_2O on the Ce surface by the measurements of the pressure and temperature dependences of the reaction rate under an ultra high vacuum condition.

2. Experimental procedure

Ce film samples with a thickness of 100 nm were deposited onto the wall of a glass sphere (reaction cell) by evaporating a block sample under an ultra high vacuum below 5×10^{-8} Pa. Before the deposition, the block sample was degassed thoroughly by heating up to 1300 K at a vacuum below 5×10^{-8} Pa. In addition, a whole glass apparatus with the glass sphere and ionization gauges were degassed. Subsequently, H_2O gas was supplied from a gas reservoir to the reaction cell. H_2O gas was produced using an ultra high purity droplet with a specific resistivity of 15 MΩ cm. The volumetric Wagener method was used to measure the amount N, the number of adsorbed gas molecules per square centimeter, and of the reaction

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probability r_{H_2O}, the ratio of adsorption rate of gas molecules to the impinging rate of gas molecules on the metal surface. In this study, the reacted gas amount of N is expressed in molecules cm^{-2} or in monolayers (ML) where 1 ML$=10^{15}$ molecules cm^{-2}. Details of the measurement method are described elsewhere [3]. During the measurement, total pressure and partial pressures were measured by B-A gauges and a quadrupole mass spectrometer (QMS), respectively. In the adsorption of H_2O on the metal surface, the change in the partial pressure of H_2 gas desorbed from the surface was measured. From this, the reaction probability r_{2H/H_2O}, and the factor β, the fraction of the H atoms dissociated from the adsorbed H_2O molecules, were calculated by the following reaction [4],

H_2O(adsorbed) $\rightarrow 2\beta H$(adsorbed or absorbed) $+$

$(1 - \beta)H_2$(desorbed) $+$ O(adsorbed)
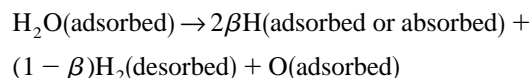
where the dissociated H atoms are assumed to be absorbed by Ce to form hydrides, and/or adsorbed to form hydroxide with the dissociated O atoms, and/or to recombine with each other and to form H_2 gas desorbing from the surface.

3. Results and discussion

3.1. Reaction kinetics

3.1.1. H_2O adsorption

Fig. 1 shows the effect of the applied H_2O pressure on the increases in the amount N_{H_2O} of H_2O adsorbed and in the amount N_{2H/H_2O} of the H atoms, that were dissociated from the adsorbed H_2O and reacted with the surface, as a function of time t, where $N_{2H/H_2O} = \beta N_{H_2O}$ is assumed. During this gas measurement, the H_2O pressure was dropped intentionally from 5.0×10^{-2} to 5.0×10^{-3} Pa at
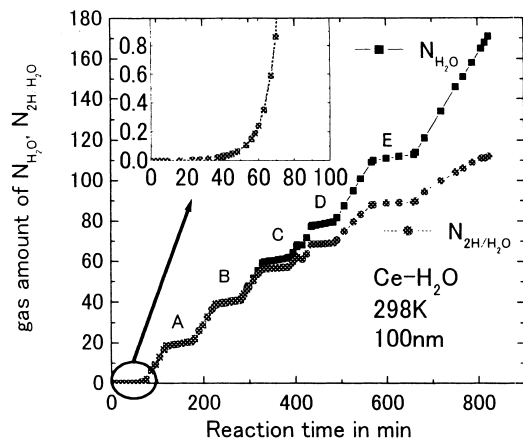
points A, B, C, D and E in Fig. 1. In the first 80 min after the start of the reaction, the pressure was increased from 10^{-8} to 5.0×10^{-2} Pa, however, the adsorption rate dN_{H_2O}/dt was very slow. When the pressure attained 5.0×10^{-2} Pa at $t=80$ min, the rate was increased. However, when the pressure was reduced at point A, the rate became slow. Similar pressure dependences of the rate were observed by changing pressure over the whole reaction. The rate was increased by a factor 10 when the pressure was raised by a factor 10 from 5.0×10^{-3} to 5.0×10^{-2}, meaning that the rate was proportional to the applied pressure, $dN_{H_2O}/dt = KP$ (k: proportional constant).

Fig. 2 shows the change in the pressure dependence of dN_{H_2O}/dt as a function of N_{H_2O}. From the measured pressure dependence, the rate controlling step of the reaction was estimated using the following equations [4,5],

$$\frac{dN}{dt} = K_1 P_R^n \exp\left(-\frac{A_e}{RT} \right) \qquad (1)$$

where N is the reacted gas amount, K is the proportional constant, P is gas pressure, n is the exponent of pressure ($0 \leq n \leq 1$), R is the gas constant, and A_e is the apparent activation energy. The meaning of n is described with respect to the rate controlling step elsewhere [5–7]. As shown in Fig. 2, the pressure dependence n of the rate was found almost $n=1$ at 298 K from the start to the end of the reaction. This result is in good agreement with the result that the rate was increased with the applied pressure as mentioned above.

3.1.2. Reactions of the H atoms from H_2O

At the initial stage ($t<200$ min or $N_{H_2O}<40$ ML in Fig. 2), the changes in dN_{H_2O}/dt and $dN_{2H/H_2O}/dt$ were found to be similar, and no H_2 desorption from the surface was observed. This means that all H_2O molecules impinging the surface reacted with the surface, and this coincides with the results of $r_{H_2O}=1$, $\beta=1$ and $r_{2H/H_2O}=1$ in Fig. 3. At this stage, all H atoms dissociated from the H_2O diffuse into Ce to form H solid solutions and then hydrides with increasing N_{H_2O}, and/or form OH layers with the O atoms

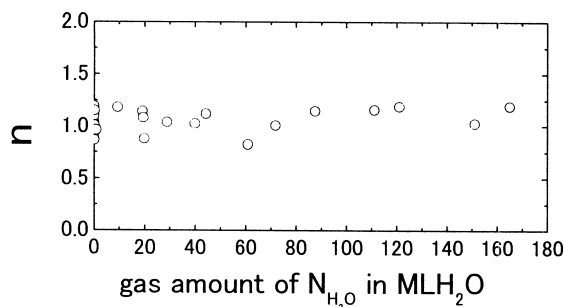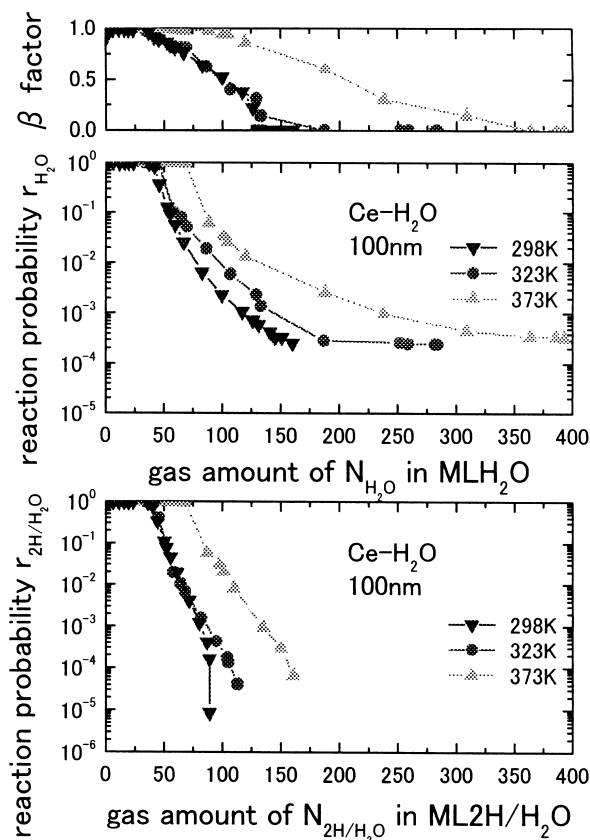Fig. 1. Pressure dependence of the rate of the H_2O amount adsorbed on the Ce surface at 298 K.

Fig. 2. Change in the pressure dependence n as a function of the H_2O amount adsorbed on the Ce surface at 298 K.

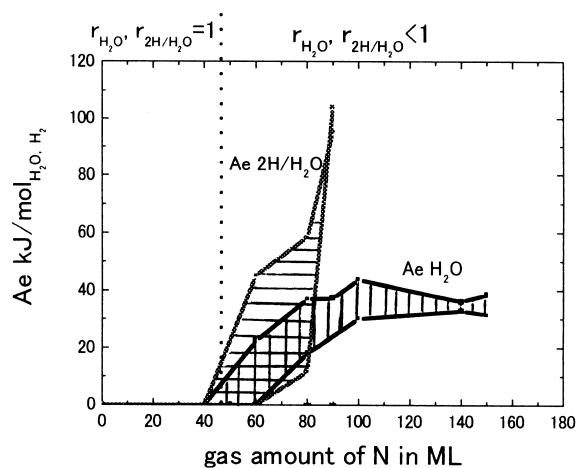Fig. 3. Temperature dependences of the reaction probabilities r_{H_2O}, r_{2H/H_2O} and β.

Fig. 4. Changes in the apparent activation energies of the H_2O adsorption and of the surface reactions of the H atoms from H_2O.

from the H_2O adsorbed on the Ce surface [2]. However, as the surface became covered with increasing amount of hydrides, oxides and/or hydroxides, $dN_{2H/H_2O}/dt$ became lower than dN_{H_2O}/dt. This indicates that surface reactions of the H atoms became inhibited by the surface oxides and/or hydroxides. The drastic drop of r_{2H/H_2O} with increasing N_{H_2O} can be seen in Fig. 3.

3.2. Temperature dependence

Fig. 3 shows the temperature dependence of r_{H_2O}, β and r_{2H/H_2O} at temperatures of 298, 323 and 373 K. At the initial stage, $r_{H_2O}=1$, $\beta=1$ and $r_{2H/H_2O}=1$ were measured at these temperatures. However, the H_2O reactivity tended to be increased as the temperature was raised, and the length of the plateaus of $r_{H_2O}=1$, $\beta=1$ and $r_{2H/H_2O}=1$ were extended. This indicates that the rate of the H_2O adsorption on the Ce surface can be accelerated effectively by increasing temperature.

With increasing temperature and the increasing N_{H_2O}, r_{H_2O} exhibited moderate drops, while r_{2H/H_2O} dropped sharply. From these temperature dependences of r_{H_2O} and r_{2H/H_2O}, the apparent activation energies A_e for the H_2O adsorption and for the surface reactions of the H atoms

form H_2O were obtained using the Eq. (1). The changes in A_e as a function of N_{H_2O} are shown in Fig. 4. The activation energies were almost zero at $r_{H_2O}=1$ and $r_{2H/H_2O}=1$ and $N_{H_2O}<40$ ML, suggesting that no thermal activation process is present. However, A_e became steeply increased at $r_{H_2O}<1$. The A_e for the H_2O adsorption was increased up to about 40 kJ (mol $H_2O)^{-1}$ and then became almost constant with increasing $N_{H_2O}<150$ ML and the A_e for the surface reactions of the H atoms exhibited a drastic increase over 100 kJ (mol $H_2)^{-1}$. These results suggest that the H_2O adsorption proceeds easier than the surface reactions of the H atoms even after the increased surface coverage of H_2O. The surface reactions of H atoms from H_2O become strongly inhibited, and then the recombination of the H atoms and the consequent desorption of H_2 gas from the surface become active as $\beta \to 0$. This means that the surface reactions of hydrogen absorption or hydride formation becomes inhibited.

4. Conclusion

The rate of the H_2O adsorption on the Ce surface is found to exhibit a pressure dependence $n=1$ at 298 K and H_2O pressures below 10^{-4} Pa. This suggests that the rate controlling step is the dissociation of H_2O. At an increased amount of adsorbed H_2O and at $r_{H_2O}<1$, the H_2O adsorption proceeds at lower activation energies than the surface reactions of the H atoms from the adsorbed H_2O, indicating a relatively ready adsorption of H_2O on the surface precovered with H_2O. However, the surface reactions of the H atoms from H_2O becomes strongly inhibited by the formation of oxide and/or hydroxide layers, resulting in a marked desorption of H_2 gas from the surface by the recombination of the H atoms.

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