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Effect of O₂ Preadsorption on the Rate of H₂ Absorption on the Surface of Rare Earths (La, Ce, Pr, Nd, Gd, Tb, Dy and Y) at 298K

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Abstract
Rare earths (RE) thin film with a clean surface was prepared under an ultra high vacuum condition. The reactivities of H₂ and O₂ with the La, Ce, Pr, Nd, Gd, Tb, Dy and Y surface were quantitatively measured by a volumetric method at pressures ranging from 10⁻⁸ to 10⁻² Pa at 298 K. At the initial stage, a clean surface of RE exhibited the highest reactivity in the reaction probability \( r = 1 \) for H₂, and O₂ respectively. As the amount of O₂ preadsorption layers was increased, \( r_{\text{H}_2} \) was decreased. The oxidized Ce surface exhibits the highest H₂ reactivity among other rare earths with oxide layers.

1 Introduction
Rare earths (RE) are widely used as constitutional elements of various functional materials, devices and catalyses. However, RE have high reactivities with H₂, O₂ and H₂O gases even at room temperature. Especially, the formation of stable surface oxides/hydroxides is one of the serious problems in the production and the use of RE containing materials. Some RE oxides like Ce oxide are used as catalysis where the Ce oxides remain still metallic even with a high coverage of surface oxide.

We have investigated the reactivities of H₂, O₂ or H₂O with the clean surface of RE using ultra high vacuum technique [1, 2]. Based on our experience, we aimed to compare some RE in the effect of preoxidation on successive hydrogen reactivity. In this study, we measured systematically the effect of O₂ preadsorption layers on the H₂ reactivity of RE (La, Ce, Pr, Nd, Gd, Tb, Dy and Y) under ultra high vacuum condition. And the H₂ reactivity on the RE surface covered with oxide layers is compared at 298 K for various RE elements.

2 Experimental Procedure
The reaction probability \( r \), defined by the ratio of the rate of reacted gas molecules to the rate of impinging by the gases on the surface, was volumetrically determined by means of Wagener method [3]. The Each block sample of a RE metal (La, Ce, Pr, Nd, Gd, Tb, Dy, Y) was carefully degassed in ultra high vacuum by increasing its temperature stepwise until 1300K where the total pressure of the system achieved less than 1×10⁻⁷ Pa. H₂ gas with a grade of 99.999999% or O₂ gas with a purity 99.99% were supplied through a hot Pd or a hot Ag diffusion cell. The reaction probability was calculated as a function of the amount of
coverage in a monolayer (ML) scale. More detailed information concerning the applied method is described elsewhere [3, 4].

3 Results and Discussion

3.1 RE metals–H\textsubscript{2} systems

As shown in Figs. 1(a) and (b), at the initial stage, the highest reaction probability, $r=1$, was observed for $\text{H}_2$ molecule. As shown in Figure 1(a), $r_{\text{H}_2}=1$ holds at the initial stage of the $\text{H}_2$ absorption by these metals. At this initial stage, the H solid solution phase may be formed for each system. In the reaction with $\text{H}_2$ at $N_{\text{H}_2} > 1$, the decrease in $r_{\text{H}_2}$ seems to be ascribed to the segregation of the dihydride phase from saturated hydrogen solid solution, and then to slower diffusion rate of H atoms inside the surface dihydride, and also to the retarded dissociation rate of $\text{H}_2$ molecules on the dihydride. Since the $\text{H}_2$ dissociation pressures of the dihydride of La, Ce, Pr, Nd, Gd, Tb, Dy and Y are lying at very low levels such $10^{-22}$ to $10^{-30}$ Pa at 298 K [2, 6], the dihydride phase of these metals can easily be formed at $\text{H}_2$ gas pressures higher than $10^{-8}$–$10^{-6}$ Pa in this experimental condition.

As shown Figure 1 (b), with increasing H concentration, $r_{\text{H}_2}$ gradually decreased until $N_{\text{H}_2}=300\times10^{15}$ molecules cm$^{-2}$ where two phases of H solid solutions and dihydride may coexist in the film samples.

The $\text{H}_2$ reaction probability $r_{\text{H}_2}$ with Ce is lying lower by an order of magnitude than those of the other metals. This may be caused because the $\text{H}_2$ equilibrium pressure for the Ce–H system is the highest among the systems [2, 6].

3.2 RE metals–O\textsubscript{2} systems

Figure 2 shows the change in the $\text{O}_2$ reactivity $r_{\text{O}_2}$ with La, Ce, Pr, Nd, Gd, Tb, Dy, and Y at 298 K as a function of the amount of adsorbed $\text{O}_2$ molecules $N_{\text{O}_2}$. At the initial stage, all samples exhibited $r_{\text{O}_2}=1$. Particularly, Ce exhibited a longer plateau at $r_{\text{O}_2}=1$, meaning the highest $\text{O}_2$ reactivity compared with the other rare earths examined in this study.

3.3 Effect of $\text{O}_2$ preadsorption

Figure 3 shows the effect of the $\text{O}_2$ preadsorption layer on the $\text{H}_2$ reactivity for La, Ce, Pr, Nd, Gd, Tb, Dy, and Y. Each film surface was precovered with $\text{O}_2$ in the ranges of the precoversages from 28 MLO$_2$ to 230 MLO$_2$.

Generally, surface oxide layers strongly hinder the dissociation of $\text{H}_2$ molecules, and subsequent H absorption [6]. However, a Ce surface with the highest amount of the $\text{O}_2$ preadsorption layers, 230 ML, exhibits the highest $r_{\text{H}_2}$ among these metal samples with $\text{O}_2$ preadsorption layers. This suggests that Ce oxides remain metallic, and can dissociate $\text{H}_2$ molecules by exchanging electrons between the surface and the molecules.

As shown in Figure 4, the influence of the Ce oxide deteriorates than the clean surface, however, the reactivity of hydrogen exhibits much higher in comparison with the other rare earths with lower amounts of oxide surfacelayers. This is a unique phenomenon to be found in only for Ce, and it is thought that a Ce oxide leaves a metallic property from this result.
Figure 1: Change in the reaction probabilities $r_{H_2}$ on the La, Ce, Pr, Nd, Gd, Tb, Dy and Y surface as a function of the reacted amount of $N_{H_2}$ of $H_2$ molecules. (a) $N_{H_2} < 1$ML (b) $N_{H_2} < 500$ML.
Figure 2: Change in the reaction probabilities $r_{O_2}$ on the La, Ce, Pr, Nd, Gd, Tb, Dy and Y surface as a function of the reacted amount of $N_{O_2}$ of $O_2$ molecules.

Figure 3: Effect of $O_2$ preadsorptions on the $H_2$ reaction probability $r_{H_2}$ on the La, Ce, Pr, Nd, Gd, Tb, Dy and Y surface as a function of the reacted amount of $N_{H_2}$ of $H_2$ molecules.
Figure 4: Effect of O₂ preadsorptions on the H₂ reaction probability $r_{H₂}$ on the Ce surface as a function of the reacted amount of $N_{H₂}$ of H₂ molecules.

4 Conclusion

At the initial stage, the highest reaction probability, $r=1$, was observed for the reactivity of H₂ and O₂ molecule on RE (La, Ce, Pr, Nd, Gd, Tb, Dy, and Y) surface at 298 K. This means that all molecules can dissociate by fast dissociation of covalent H₂ and O₂ molecules on a clean RE surface. The oxidized Ce surface exhibits the highest H₂ reactivity among the other oxidized rare earths examined, indicating the strong metallic features of the CeOₓ in comparison with the oxides of La, Pr, Nd, Gd, Tb, Dy, and Y.

References