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 H_2 and O_2, 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 H_2, and O_2 respectively. As the amount of O_2 preadsorption layers was increased, r_{H2} was decreased. The oxidized Ce surface exhibits the highest H_2 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 H_2 , O_2 and H_2O 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 H_2, O_2 or H_2O 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 O_2 preadsorption layers on the H_2 reactivity of RE (La, Ce, Pr, Nd, Gd, Tb, Dy and Y). under ultra high vacuum condition. And the H_2 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. H_2 gas with a grade of 99.99999% or O_2 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_2 systems

As shown in Figs. 1(a) and (b), at the initial stage, the highest reaction probability, r=1, was observed for H_2 molecule. As shown in Figure 1(a), r_{H2}=1 holds at the initial stage of the 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 H_2 at $N_{H2} > 1$, the decrease in r_{H2} 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 H_2 molecules on the dihydride. Since the 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 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_{H2} gradually decreased until N_{H2}=300×10^{15} molecules cm^{-2} where two phases of H solid solutions and dihydride may coexist in the film samples.

The H_2 reaction probability r_{H2} with Ce is lying lower by an order of magnitude than those of the other metals. This may be caused because the H_2 equilibrium pressure for the Ce–H system is the highest among the systems [2, 6].

3.2   RE metals–O_2 systems

Figure 2 shows the change in the O_2 reactivity r_{O2} with La, Ce, Pr, Nd, Gd, Tb, Dy, and Y at 298 K as a function of the amount of adsorbed O_2 molecules N_{O2}. At the initial stage, all samples exhibited r_{O2}=1. Particularly, Ce exhibited a longer plateau at r_{O2}=1, meaning the highest O_2 reactivity compared with the other rare earths examined in this study.

3.3   Effect of O_2 preadsoption

Figure 3 shows the effect of the O_2 preadsorption layer on the H_2 reactivity for La, Ce, Pr, Nd, Gd, Tb, Dy, and Y. Each film surface was precovered with O_2 in the ranges of the precoverages from 28 MLO_2 to 230 MLO_2.

Generally, surface oxide layers strongly hinder the dissociation of H_2 molecules, and subsequent H absorption [6]. However, a Ce surface with the highest amount of the O_2 preadsorption layers, 230 ML, exhibits the highest r_{H2} among these metal samples with O_2 preadsorption layers. This suggests that Ce oxides remain metallic, and can dissociate 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.
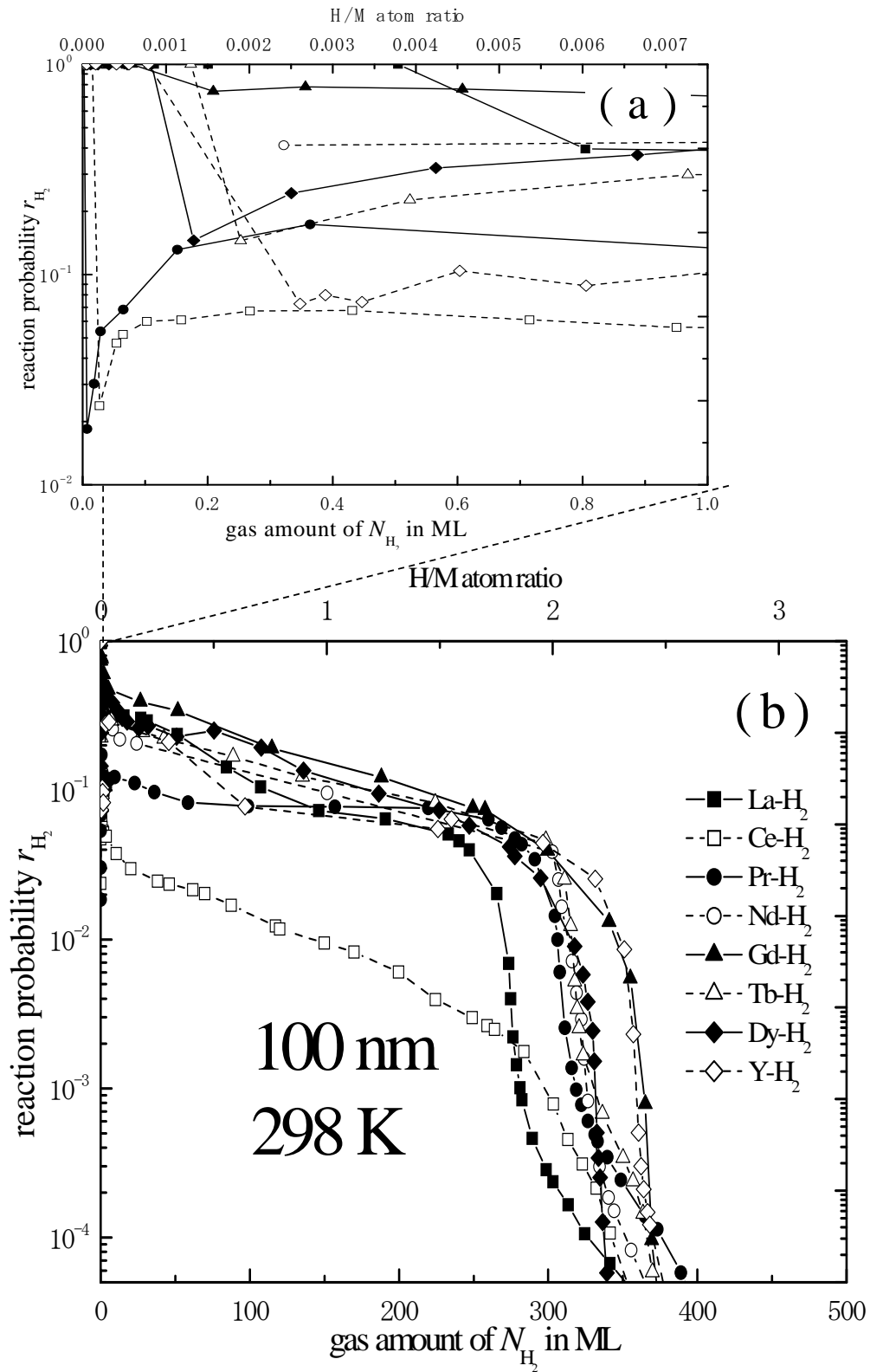
Figure 1: Change in the reaction probabilities r_{H2} on the La, Ce, Pr, Nd, Gd, Tb, Dy and Y surface as a function of the reacted amount of N_{H2} of H_2 molecules. (a) N_{H2} < 1ML (b) N_{H2} <500ML.
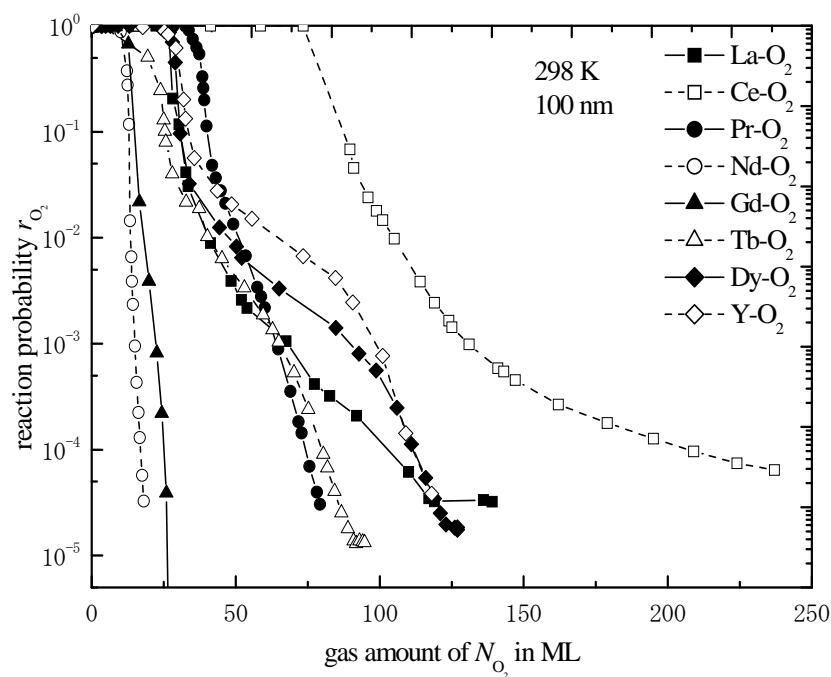
Figure 2: **Change in the reaction probabilities r_{O2} on the La, Ce, Pr, Nd, Gd, Tb, Dy and Y surface as a function of the reacted amount of N_{O2} of O_2 molecules.**
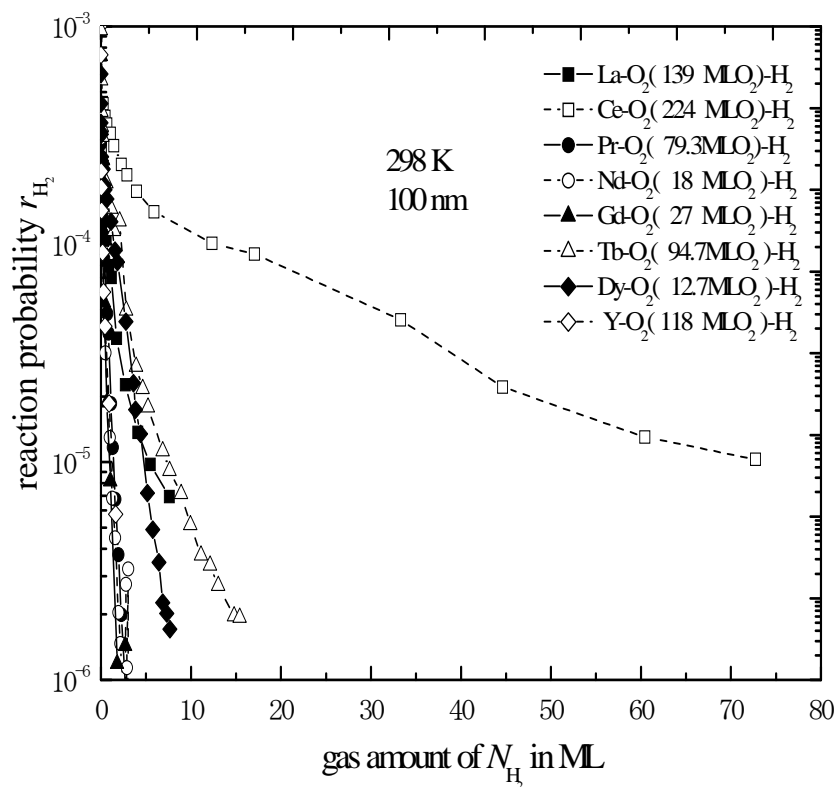

Figure 3: **Effect of O_2 preadsorptions on the H_2 reaction probability r_{H2} on the La, Ce, Pr, Nd, Gd, Tb, Dy and Y surface as a function of the reacted amount of N_{H2} of H_2 molecules.**
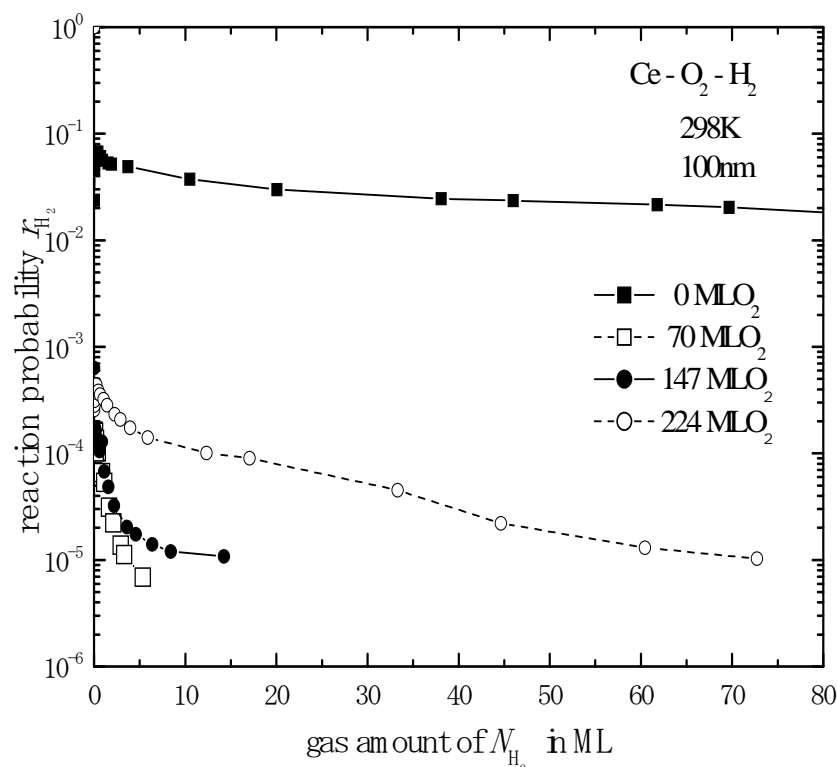
Figure 4: Effect of O_2 preadsorptions on the H_2 reaction probability r_{H2} on the Ce surface as a function of the reacted amount of N_{H2} of H_2 molecules.

4   Conclusion

At the initial stage, the highest reaction probability, $r=1$, was observed for the reactivity of H_2 and O_2 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 H_2 and O_2 molecules on a clean RE surface. The oxidized Ce surface exhibits the highest H_2 reactivity among the other oxidized rare earths examined, indicating the strong metallic features of the CeO_x in comparison with the oxides of La, Pr, Nd, Gd, Tb, Dy and Y.

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