Photocatalytic Decomposition of Pure Water over NiO Supported on $KTa(M)O_3$ ($M=Ti^{4+},Hf^{4+},Zr^{4+}$) Perovskite Oxide

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Photocatalytic decomposition of pure water on NiO supporting $KTaO_3$ partially substituted with acceptor was investigated. Formation rate of H_2 and O_2 increased by partially substituting Ta with group 4 element. The increased photocatalytic decomposition activity by additives might be caused by a charge carrier annihilation.

Hydrogen is an important molecule not only as a clean energy source but also an important chemical reagent. Development of a H_2 production method with small energy consumption is strongly required at present. Photolysis of water is an attractive method, since a simple apparatus is enough and the energy input become small by using solar light. Therefore, the photolysis of water has been studied extensively and various semiconductors, mainly, Ti and Nb based oxide, are reported as a catalyst for H_2O photolysis.[1-4] In particular, Sayama et al. investigated photolysis on Ta based oxide.[2] On the other hand, number of the catalyst, which produces H_2 and O_2 at a stoichiometric ratio to H_2O decomposition, has been limited up to now.[1-3] In our previous work, it was found that the activity of $KTaO_3$ to the photolysis of water was greatly improved by partially substituting Ta with Zr^{4+}, Hf^{4+}, or Ti^{4+}. In particular, H_2 and O_2 at the stoichiometric ratio to H_2O decomposition was formed on $NiO/KTa_{0.92}Zr_{0.08}O_{2.96}$.[5] Except for Zr^{4+}, photocatalytic activity of Ti^{4+} and Hf^{4+} added catalyst have not been thoroughly studied. In this study, effect of Hf^{4+} and Ti^{4+} doping to $KTaO_3$ on the activity to the photolysis of H_2O was investigated in detail. Effect of ionic size of additives on H_2O photolysis activity was further studied.

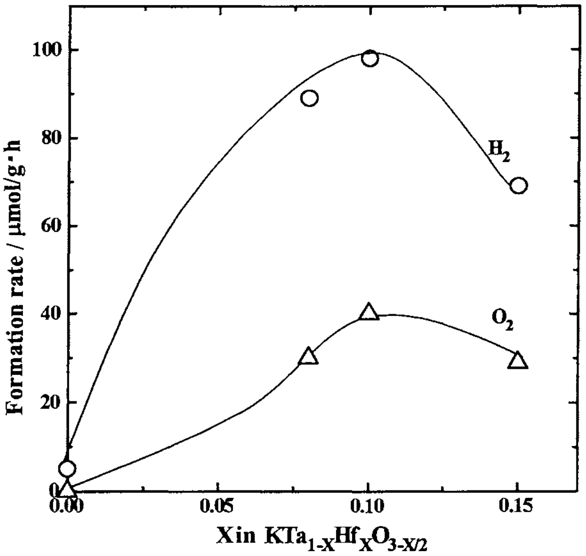

Figure 2. Formation rate of H_2 and O_2 as a function of Hf content in $KTaO_3$ (1 wt% NiO loaded).

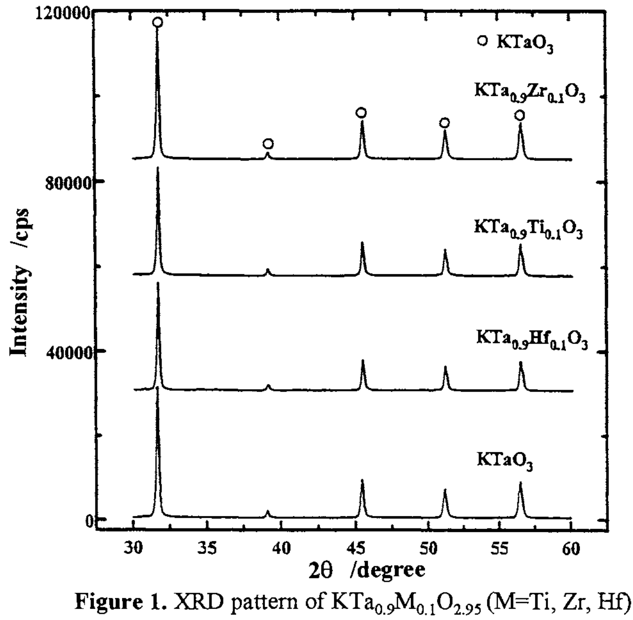

Figure 1. XRD pattern of $KTa_{0.9}M_{0.1}O_{2.95}$ (M=Ti, Zr, Hf).

$KTaO_3$ substituted with Ti^{4+} or Hf^{4+} were always prepared by the conventional solid solution method. Stoichiometric mixture of Ta_2O_3 (Kishida 99.9%), alkaline carbonate, and a commercial metal oxide (Wako 99.9%) was calcined at 1273 K in air for 10 h. Loading nickel oxide on the doped $KTaO_3$ was performed by an impregnation method with a $Ni(NO_3)_2$ aqueous solution. Thus prepared catalyst was reduced in flowing H_2 (773 K for 2 h) and then reoxidized in flowing O_2 (473 K for 2 h). The photocatalytic decomposition of water was performed with a closed circulating system and argon gas was used as a carrier gas. The catalyst powder (100 mg) was suspended to the commercial deionized water (Takasugi, 30 cm^3). Pyrex reaction cell was irradiated by an external light source of a 500 W xenon lamp (Ushio). Hydrogen and oxygen formed by the photolysis of H_2O were measured with a TCD gas chromatograph connected to a circulating line. The formation rate of H_2 and O_2 was estimated within the first few hours by assuming a first order reaction.

Figure 1 shows XRD patterns of the prepared $KTa_{0.9}M_{0.1}O_{2.95}$ (M = Hf, Ti). Since all diffraction peaks were assigned to that of $KTaO_3$, doped tetravalent cations of Hf and Ti seems to partially substitute Ta in $KTaO_3$. Formation rate of H_2 and O_2 was shown in Figure 2 as a function of the amount of Hf^{4+} doped for the Ta site of $KTaO_3$. It is obvious that the formation rate of H_2 and O_2 increased with increasing the amount of doped Hf^{4+} and it attained to a maximum value at X=0.1 in $KTa_{1-X}Hf_XO_{3-X/2}$. At this composition, the formation rate of H_2 and O_2 attained values of 98 and 40 $\mu molg^{-1}h^{-1}$ respectively, which is higher than that of $KTa_{0.92}Zr_{0.08}O_{2.96}$.

Figure 3 showed the formation rate of H_2 and O_2 as a

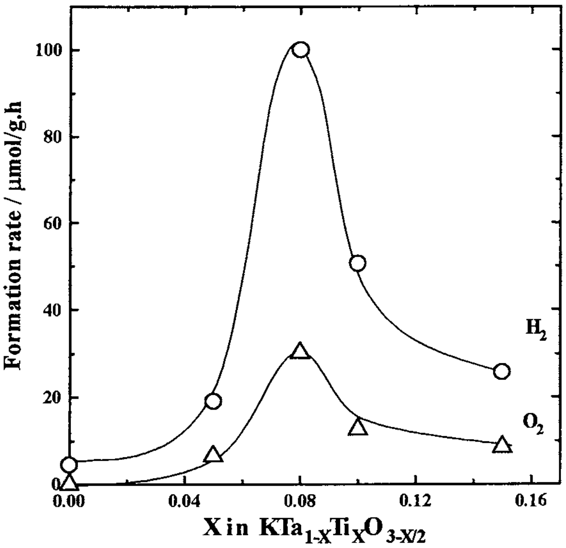

Figure 3. Formation rate of H_2 and O_2 as a function of Ti content in $KTaO_3$ (1 wt% NiO Loaded).

function of the amount of Ti^{4+} substituting Ta site of $KTaO_3$. In a similar manner with doping Hf^{4+} or Zr^{4+}, the formation rate of H_2 and O_2 increased with increasing the amount of doped Ti^{4+} attaining to the maximum value at X=0.08. Therefore, it is clear that doping Ti^{4+} was also effective for increasing the activity to H_2O photocatalytic decomposition. In particular, formation rate of H_2 at the optimized composition of X=0.08 reached to a value of 100 μmolg^{-1}h^{-1} which is higher than those of Zr^{4+} or Hf^{4+} added ones, while the formation rate of O_2 was slightly lower than half of H_2 formation rate. This was not anticipated from our previous study.[5] As a result, it can be said that NiO loading $KTaO_3$ partially substituted with group 4 elements exhibit high activity to H_2O photocatalytic decomposition. Although these effects by additives appeared in a narrow composition range, the reproducibility in formation rate was satisfactorily high.

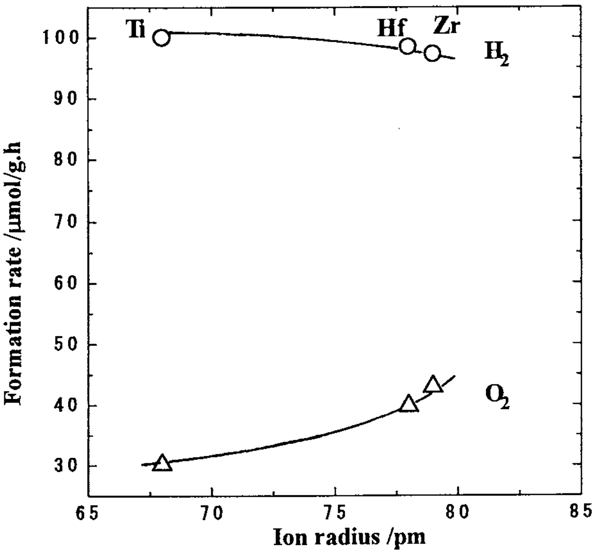

Figure 4. Formation rate of H_2 and O_2 as a function of ion radius of doping cation to $KTaO_3$.

The formation rate of H_2 and O_2 at the optimized composition for each additive was plotted in Figure 4 against the ionic radius of six coordination. It is also noted that the ionic radius of six coordinated Ta^{5+} is 68pm which is slightly smaller than that of all additives. Obviously, the formation rate of H_2 tends to decrease with increasing the ionic radius of the doped cations, but that of O_2 exhibited the opposite dependency. Namely, formation rate of O_2 was increased with increasing ionic radius of additive. XPS measurement suggested that oxygen species of which electronic state is different from that of lattice oxygen, formed by doping Zr. Since it is expected that the local stress in the lattice is formed by the introduction of larger sized cations, it seems likely that the desorption of oxygen became easier with increasing ionic radius of dopant.[6] Therefore, almost stoichiometric amount of oxygen was formed on the catalyst added with Zr^{4+} or Hf^{4+}. The similar mechanism for the formation of oxygen in photolysis of H_2O is proposed by Inoue et al.[3] On the other hand, UV-Vis spectra suggest that doping Hf^{4+}, Ti^{4+}, or Zr^{4+} caused no significant change in the band gap (ca.3.8 eV) of $KTaO_3$. However, electrical conductivity decreased by substituting Ta with group 4 element. Therefore, it seems most likely that these group 4 elements work as a charge carrier annihilator and it is expected that the life of photo excited electron and hole is improved by decreasing charge density. Consequently, H_2 formation rate was greatly improved by partially substituting Ta with group 4 elements. On the other hand, carrier density would become insufficient by adding the excess amount of an annihilator. Therefore, the activity decreased by addition of excess amount of group 4 element. Any way, this study reveals that all group 4 elements are highly effective for increasing the activity of NiO loading $KTaO_3$ for H_2O photocatalytic decomposition.

References

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