

Novel Photocatalysts, Ion-exchanged $K_4Nb_6O_{17}$, with a Layer Structure

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Proton-exchanged $K_4Nb_6O_{17}$ showed high activity for H_2 evolution from aqueous methanol solution without any assistance from other materials such as noble metals.

Photocatalytic reactions over semiconductors such as TiO_2 , CdS, and $SrTiO_3$ have been studied by many workers.¹ Recently we have reported that $K_4Nb_6O_{17}$ photocatalyst exhibits high activity for H_2 evolution from aqueous methanol solution and that a pretreated NiO (0.1 wt%)– $K_4Nb_6O_{17}$ photocatalyst can decompose H_2O into H_2 and O_2 stoichiometrically.² $K_4Nb_6O_{17}$ has a layer structure,³ and separating the layers are two types of interlayers. One type of interlayer contains water molecules and potassium ions and the other contains only potassium ions. The potassium ions

between niobium oxide layers can be replaced with many other cations including transition metal ions.⁴ We report here that among ion-exchanged $K_4Nb_6O_{17}$ photocatalysts, $H^+/K_4Nb_6O_{17}$ shows the highest photocatalytic activity for H_2 evolution from aqueous methanol solution. As far as we know, this is the first example of a metal oxide which shows high and stable activity for H_2 evolution without any assistance from other materials such as noble metals, although ZnS is also known to have a similar high activity for H_2 evolution.⁵

$K_4Nb_6O_{17}$ was prepared by calcination of a mixture of

Table 1. H₂ evolution from aqueous methanol solution over ion-exchanged K₄Nb₆O₁₇.^a

Exchanged ions	% Exchanged K ⁺	H ₂ /μmol h ⁻¹
None	0	30
H ⁺	51	251
Cr ³⁺	66	101
Fe ³⁺	70	109
Co ²⁺	40	0
Ni ²⁺	23	3
Cu ²⁺	60	0

^a Catalyst: 0.5 g; light source: Xe lamp (500 W); solution: MeOH-H₂O (1:4 v/v), 250 ml. Catalysts were dried at 120 °C.

K₂CO₃ and Nb₂O₅ at 1573 K in air and its structure was confirmed by X-ray diffraction.⁶ The surface area of the oxide was smaller than 1 m² g⁻¹ by Brunauer-Emmett-Teller measurement.

Ion-exchanged niobates were prepared by the exchange reaction between K⁺ and H⁺ in H₂SO₄ (hereafter referred to as H⁺/K₄Nb₆O₁₇) or transition metal ions in aqueous metal nitrate solutions (Mⁿ⁺/K₄Nb₆O₁₇) at room temperature. The amount of exchanged K⁺ was determined by detection of the amount of K⁺ eluted into solution using an atomic absorption measurement. It was found by X-ray diffraction methods that the layer structure was maintained although the distance between the layers changed slightly after the ion-exchange reaction. The catalyst was suspended in a solution (250 ml) of MeOH and H₂O (1:4 v/v) using a magnetic stirrer. The solution was degassed in a closed gas circulation system and reactions were carried out under an Ar (*ca.* 100 torr) atmosphere. An Xe lamp (USHIO, 500 W) was used as a light source. The amounts of H₂ and CO₂ evolved were determined by gas chromatography (thermal conductivity detector, Ar carrier, molecular sieve 5 Å column).

In Table 1, the amount of exchanged K⁺ and the activities of photocatalytic H₂ evolution from aqueous methanol solution over ion-exchanged K₄Nb₆O₁₇ are shown. The H⁺-exchanged K₄Nb₆O₁₇ showed the highest activity for H₂ evolution without noble metals such as Pt. The quantum efficiency was around 30% at 330 nm by chemical actinometry. Of the

transition metal ions used, the activities of catalysts exchanged with Cr³⁺ and Fe³⁺ were higher than that of original K₄Nb₆O₁₇, while catalysts exchanged with Co²⁺, Ni²⁺, and Cu²⁺ showed very low activities. In some cases the ion-exchanged catalysts may partly contain H⁺ instead of transition metal ions. When the K₄Nb₆O₁₇ photocatalyst exchanged with H⁺, Fe³⁺, or Cr³⁺ was calcined at 773 K in air it shows almost no activity. In this case it was found by X-ray diffraction methods that the original layer structure was broken by calcination.

On the H₂ evolution reaction from aqueous methanol solution over H⁺/K₄Nb₆O₁₇, the catalyst shows constant activity for more than 16 h and the amount of evolved H₂ (3820 μmol) for 16 h is about one order of magnitude greater than the amount of protons (*ca.* 200 μmol as H₂) incorporated into K₄Nb₆O₁₇ (0.2 g) by ion-exchange. No dark reaction was observed. These facts lead us to conclude that H₂O in the reactant is reduced photocatalytically to H₂. Methanol was mainly oxidized to form CO₂ in the gas phase during the reaction. Although Pt was reduced to metallic platinum, no enhancement of the activity was observed by adding H₂PtCl₆ to the H⁺/K₄Nb₆O₁₇ system which is different from the TiO₂ and SrTiO₃ systems. When light of wavelength shorter than 370 nm is used H⁺/K₄Nb₆O₁₇ shows photocatalytic activity. This means that the band gap of this material is estimated to be *ca.* 3.3 eV, and also that the conduction band level should be negative compared with the H⁺/H₂ redox potential.

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