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A NOVEL SERIES OF PHOTOCATALYSTS WITH AN ION-EXCHANGEABLE LAYERED STRUCTURE OF NIOBATE

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Ion-exchangeable niobates, $A(M_{n-1}Nb_nO_{3n+1})$ (A = Na, K, Rb, Cs; M = La, Ca etc.), with a layered perovskite structure are found to show a unique photocatalytic activity, especially in those H^+-exchanged forms, for H_2 evolution from aqueous alcohol solutions as well as O_2 evolution from an aqueous silver nitrate solution.

1. Introduction

Some ion-exchangeable niobates with a layered perovskite structure were found to be a new class of heterogeneous photocatalysts due to the unique structure of those materials, and were suggested to work as "two-dimensional" photocatalysts in which catalytic reactions mainly proceed at the interlayer spaces.

Recently we reported that some ion-exchangeable layered compounds showed a noticeable photocatalytic activity. Especially, $A_4Nb_6O_{17}$ (A = K or Rb) loaded with Ni metal exhibited high and stable activity for overall water splitting into H_2 and O_2 [1, 2], and it was inferred that intercalated water molecules are decomposed into H_2 and O_2 at the interlayer spaces of $A_4Nb_6O_{17}$ in these catalysts.

This paper will report other types of layered compounds as photocatalysts, which are classified in the layered perovskite family. These compounds are generally formulated as $A(M_{n-1}Nb_nO_{3n+1})$ (A = Na, K, Rb, Cs; M = La, Ca, etc.) [3–7]. For example, $ALaNb_2O_7$ and $ACa_2Nb_3O_{10}$ are the members of $n = 2$ and 3, respectively, as shown in fig. 1. Alkaline metal ions at the interlayers can be replaced by other cations. Especially in acidic solution, almost 100% of alkaline

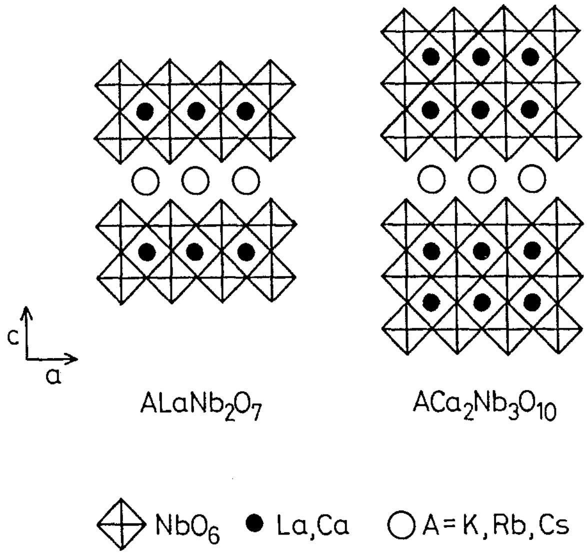

Fig. 1. Schematic structures of $ALaNb_2O_7$ and $ACa_2Nb_3O_{10}$ (A = K, Rb, Cs).

metal ions are exchanged by H^+ ions. The H^+-exchanged forms of those compounds are easily hydrated while the original ones are not.

2. Experimental

Catlysts were prepared according to the previous publications [3–7]. $ALaNb_2O_7$ was prepared by calcination of stoichiometric mixture of A_2CO_3, La_2O_3 and Nb_2O_5 at 1200 °C for 2 days in air. $ACa_2Nb_3O_{10}$ and $ASr_2Nb_3O_{10}$ were obtained from mixture of A_2CO_3, $CaCO_3$, Nb_2O_5 and A_2CO_3, $SrCO_3$, Nb_2O_5, respectively, following the similar procedure of $ALaNb_2O_7$. After calcination, the solid products were washed with distilled water and dried in air at room temperature. The structure of those products were confirmed by X-ray diffraction which coincided with those in the literature [3–7]. The catalyst powders were 1–10 μm in diameter. The photocatalytic H_2 evolution from aqueous methanol solution and O_2 evolution from aqueous silver nitrate solution over these compounds was examined under irradiation of a high pressure Hg lamp (450 W). H^+-exchange was carried out in 5 N HNO_3 solution for 3 days at room temperature.

3. Results and discussion

The rates of H_2 and O_2 evolutions are summarized in table 1 as well as the band gaps estimated from diffuse reflectance spectra. The results of $K_4Nb_6O_{17}$ and TiO_2 are also shown for reference. Pt loading was carried out by a photode-

Table 1
Photocatalytic activities of layered perovskite compounds; A $(M_{n-1}Nb_nO_{3n+1})$

Catalyst	n	rate of gas evolution/$\mu mol \cdot h^{-1}$					band gap energy/eV
		H_2 [a]				O_2 [b]	
		original		H^+-exchanged [c]			
		alone	Pt-loaded [d]	alone	Pt-loaded [d]		
$K_4Nb_6O_{17}$ [e]	1	130	270	750	740	13	3.5
$KLaNb_2O_7$	2	28	54	760	3800	46	3.2
$RbLaNb_2O_7$	2	60	90	740	2600	2	3.35
$CsLaNb_2O_7$	2	12	28	300	2200	3	3.3
$KCa_2Nb_3O_{10}$	3	14	100	5900	19000	8	3.35
$RbCa_2Nb_3O_{10}$	3	3	26	3100	17000	16	3.5
$CsCa_2Nb_3O_{10}$	3	2	10	970	8300	10	3.5
$KSr_2Nb_3O_{10}$	3	10	110	8900	43000	30	3.16
$KCa_2NaNb_4O_{13}$	4	5	280	790	18000	39	3.21
TiO_2 [f]	–	–	7400	–	–	660	3.0

Catalyst: 1 g, Hg lamp (450 W), [a] CH_3OH 50 ml+H_2O 300 ml, [b] 0.01 M $AgNO_3$aq. 350 ml, [c] H^+-exchange degreee >95%, [d] 0.1 wt% of Pt loading, [e] layered orthorhombic structure, [f] anatase, purchased from MCB.

position method with addition of H_2PtCl_6 into the aqueous methanol solution [8]. Although all layered compounds showed moderate activity for H_2 evolution in those original forms, marked enhancement of the H_2 evolution rate by two or three orders of magnitude were observed by the replacement of alkaline metal ions with H^+ ions. Further increase of the activity by several times occurred with the loading of Pt in each case. Since these layered compounds work as cation-exchanger, $PtCl_6^{2-}$ ions are difficult to intercalate into interlayer spaces of the catalyst; i.e. photo-deposited Pt particles are expected to exist at the external surface of the catalyst. It should be emphasized that Pt loading is not an indispensable condition for efficient H_2 evolution, which is unlike the cases of TiO_2, CdS and so on. The activities were stable over about a 10 h period and the total amounts of evolved H_2 exceeded the equivalent amounts of used catalysts which confirmed the catalytic cycle of the reaction for every H^+-exchanged form.

As is mentioned above, H^+-exchanged forms of these compounds are hydrated and the c-axis lengths corresponding to the interlayer spacing increase with hydration. The marked increase of the H_2 evolution rates, therefore, is considered to be due to the migration of the reactants, i.e. H_2O and CH_3OH, into the interlayer spaces. To examine this speculation, the dependence of the H_2 evolution rate on the degree of H^+-exchange for $KCa_2Nb_3O_{10}$ in aqueous methanol solution was studied. As shown in fig. 2, the rate of H_2 evolution increased drastically with H^+-exchange degree of ca. 60%. From XRD measurements, the interlayer space length (c-axis) was found to be expanded by ca. 0.8 Å at the same degree of H^+-exchange. This structural change is caused by an increase of

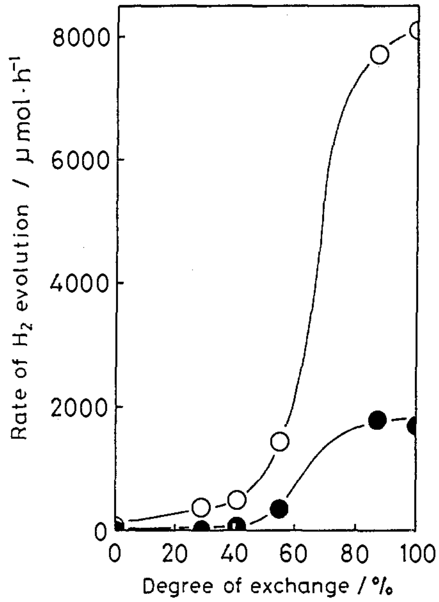

Fig. 2. Dependence of H_2 evolution rate on the degree of H^+-exchange over $H^+/KCa_2Nb_3O_{10}$ and Pt(0.1 wt%) – $H^+/KCa_2Nb_3O_{10}$. ●; $H^+/KCa_2Nb_3O_{10}$, ○; Pt(0.1 wt%)-$H^+/KCa_2Nb_3O_{10}$. H^+-exchange was carried out in 0.1–5N HNO_3 aqueous solution for 3 days at room temperature. 450 W high pressure mercury lamp, catalyst 1 g, CH_3OH (50 ml) + H_2O(300 ml).

hydrated water molecules at the interlayer spaces and is responsible for the increase of the H_2 evolution rate. Further support for the migration of reactants into the interlayer spaces was obtained by comparing each H_2 evolution rate over H^+-exchanged $KCa_2Nb_3O_{10}$ in various kinds of alcohol solutions, as summerized in table 2 as well as the results of a reference Pt/TiO_2 catalyst. With the increase of the length of an alkyl group of alcohol from methyl to butyl, the rate of H_2 evolution decreased by more than two orders of magnitude, which may suggest that the migration of alcohol molecules into the interlayer spaces determines the reaction rate.

Table 2
Rates of H_2 evolution from various kinds of alcohol solutions ($\mu mol \cdot h^{-1}$)

alcohol	catalyst			
	$KCa_2Nb_3O_{10}$	$H^+/KCa_2Nb_3O_{10}$ [a)]	Pt-$H^+/KCa_2Nb_3O_{10}$ [a,b)]	Pt-TiO_2 [b)]
methanol	7	920	4670	4000
ethanol	7	73	384	5170
1-propanol	3	27	43	3480
1-butanol	2	19	30	2790

Catalyst: 1 g, Hg lamp (450 W), alcohol 50 ml + H_2O 300 ml, [a)] H^+-exchange degree > 95%, [b)] 0.1 wt% of Pt loading.

In aqueous $AgNO_3$ solution, O_2 evolution was observed for each layered compound under a high pressure Hg lamp irradiation as shown in table 1. It is, therefore, suggested that these layered perovskites have a possibility for overall water splitting by proper modification as in the case of $A_4Nb_6O_{17}$ (A = K, Rb). It is further noted that many derivatives of this family are can be prepared by replacing Ca^{2+}, Sr^{2+} or La^{3+} positions by other metal ions. Some of those compounds such as $KPbNb_2O_7$ and $KNdNb_2O_7$ actually show photoresponse in visible light irradiation [9] and further study is now proceeding in our laboratory.

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