ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 114 (1998) 125–135

Journal of Photochemistry and Photobiology A:Chemistry

Photocatalytic activity and reaction mechanism of Pt-intercalated $K_4Nb_6O_{17}$ catalyst on the water splitting in carbonate salt aqueous solution

K. Sayama [a], K. Yase [a], H. Arakawa [a,*], K. Asakura [b], A. Tanaka [c], K. Domen [d], T. Onishi [d]

[a] *National Institute of Materials and Chemical Research (NIMC), 1-1 Higashi, Tsukuba-City, Ibaraki 305, Japan*
[b] *Research Center for Spectrochemistry, Faculty of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan*
[c] *Nikon, 1773 Asamizodai, Sagamihara 228, Japan*
[d] *Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 227, Japan*

Received 26 August 1997; received in revised form 5 December 1997; accepted 18 December 1997

Abstract

Both the structure of Pt-intercalated $K_4Nb_6O_{17}$ catalyst and the photocatalytic activity on the water splitting in aqueous carbonate salt solution were studied using various kinds of analytical measurements such as FT-IR, EXAFS, TEM, SEM and TPR. $K_4Nb_6O_{17}$ was the layered semiconductor which have two kinds of interlayer spaces (interlayers I and II), and it was found by FT-IR that the $[Pt(NH_3)_4]^{2+}$ cation was preferentially intercalated only into the interlayer I of $K_4Nb_6O_{17}$. Fine Pt metal particles less than 6 Å (1 Å = 0.1 nm) were prepared homogeneously in the interlayer space I by the photoreduction method. By H_2 reduction, some Pt particles grew more than 15 Å and contributed to the destruction of the layered sheet. The photocatalytic water splitting reaction occurred by the addition of carbonate salt in spite of the exposure of Pt on the outer surface of catalyst. The photocatalytic activity of the $Pt/K_4Nb_6O_{17}$ prepared by the photoreduction was higher than that prepared by the H_2 reduction. The deactivation of the catalyst was not observed in the carbonate aqueous solution for long time. The reaction mechanism that the Pt particles in the interlayer I acted as H_2 evolution site and the O_2 evolved in the interlayer II was proposed.

Keywords: Photocatalyst; Decomposition of water; $K_4Nb_6O_{17}$; Pt-intercalation; Carbonate addition

1. Introduction

Many kinds of photocatalysts for the decomposition of water into H_2 and O_2 have been widely studied from the viewpoint of solar energy utilization. It was reported that Ni-intercalated $A_4Nb_6O_{17}$ (A = K, Rb) catalysts showed high activities, and these quantum efficiencies were 5–10% at 330 nm [1–4]. $A_4Nb_6O_{17}$ is a unique layered compound consisting of two kinds of interlayers (interlayers I and II) exhibiting different chemical properties [5,6]. For example, only interlayer I of $K_4Nb_6O_{17}$ can be hydrated under atmospheric conditions (humidity: 30–80%) to form $K_4Nb_6O_{17}\cdot 3H_2O$, whereas both interlayers can be hydrated in aqueous solution [7]. Moreover, K^+ ions in interlayer II can be substituted by only monovalent cations such as Na^+ and H^+, whereas K^+ ions in interlayer I can be substituted by both mono- and bivalent cations such as Ni^{2+} and Ca^{2+} [8]. The character of $Ni/K_4Nb_6O_{17}$ was examined by EXAFS, XPS and TEM, and it was found that nickel was located as very fine metal particles (ca. 5 Å) in the interlayer I [9]. Though $Ni/K_4Nb_6O_{17}$ catalyst showed a good photocatalytic activity, it had the disadvantage that the rate of gas evolution decreased with reaction time because Ni metal particles were gradually oxidized. We tested many kinds of metal-loaded $K_4Nb_6O_{17}$ catalysts for stable water splitting reaction, and it was demonstrated successfully that Pt-intercalated $K_4Nb_6O_{17}$, which was prepared by ion-exchange of $[Pt(NH_3)_4]^{2+}$ followed by H_2 reduction and aqua regia (mixture of HNO_3 and HCl) treatment to remove Pt on the external surface of $K_4Nb_6O_{17}$, showed the activity for photocatalytic water decomposition into H_2 and O_2 in a stoichiometric ratio ($H_2/O_2 = 2$) [10]. Platinum is the best material for the H_2 evolution site because of its extremely low overpotential for H_2 evolution and excellent stability; however, the activity of $Pt/K_4Nb_6O_{17}$ catalyst is smaller than that of $Ni/K_4Nb_6O_{17}$, and deactivation of $Pt/K_4Nb_6O_{17}$ catalyst is observed after long reaction time. Because the rapid backward reaction ($2H_2 + O_2 \rightarrow 2H_2O$) on

---

* Corresponding author.

1010-6030/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII S1010-6030(98)00202-0

Pt particles which remained on the external surface of catalysts even after aqua regia treatment was a very serious problem. The layered catalyst might be disrupted by vigorous stirring and the intercalated Pt particles exposed to the outside during reaction. Furthermore, the catalyst seemed to be injured by aqua regia treatment, because repetition of the treatment caused deactivation of the catalysts. The optimum amount of metal for the activity of Pt/$K_4Nb_6O_{17}$ (0.01 wt.% of Pt) was much smaller than that of Ni/$K_4Nb_6O_{17}$ (0.1 wt.% of Ni). Recently, we found that several kinds of Pt loaded catalysts showed excellent activities for the photocatalytic water decomposition with the simple expediency using highly-concentrated carbonate salt aqueous solution [11–16] thereby avoiding the need for aqua regia treatment. Here, we report remarkable advantages of the carbonate addition method on Pt/$K_4Nb_6O_{17}$ catalyst system.

In addition to the photocatalytic activity of Pt/$K_4Nb_6O_{17}$ for the water splitting, the behavior of $[Pt(NH_3)_4]^{2+}$ in the narrow interlayer on the reduction condition and the structure of Pt/$K_4Nb_6O_{17}$ are very attractive as a unique Pt catalyst. The characters of Pt/zeolite catalysts that have been prepared by ion-exchange with $[Pt(NH_3)_4]^{2+}$ have been widely studied [17–24]. The charge densities within zeolite cages were relatively low (0.01–0.03 $Å^{-2}$) and the ion-exchange capacity were very high. On the other hand, $K_4Nb_6O_{17}$ has very high charge density (0.08 $Å^{-2}$), and there is few reports concerning intercalation of large molecules such as $[Pt(NH_3)_4]^{2+}$. It is not clear which K^+ ions of the two interlayers can be replaced by $[Pt(NH_3)_4]^{2+}$. In this study, we also report a characterization study of Pt/$K_4Nb_6O_{17}$ using FT-IR, EXAFS, SEM, TEM and TPR measurement.

2. Experimental details

$K_4Nb_6O_{17}$ powder was prepared by calcination of the mixture of Nb_2O_5 (Mitsui Kinzoku) and K_2CO_3 (Asahi Glass) at 1573 K for 15 min in air. The product was crushed to small pieces (ca. 1–10 μm) in a mortar, and the crystal structure was confirmed by powder X-ray diffraction (XRD) compared to known standards [5–7]. $K_4Nb_6O_{17}$ (5.0 g) was immersed in an aqueous solution (5 ml) containing a required amount of $[Pt(NH_3)_4]Cl_2$ (NE Chemcat) for ion exchange between K^+ and $[Pt(NH_3)_4]^{2+}$ ions. The suspension was stirred magnetically for 3 days at room temperature, dried on a water bath, and washed well with distilled water to remove excess $[Pt(NH_3)_4]Cl_2$ on the external surface. Then, the sample was reduced by one of two different methods: either using a H_2 reduction or a photoreduction. H_2 reduction was undertaken in a closed gas-circulation system with H_2 (ca. 400 Torr, 1 Torr = 133.3 N m^{-2}) at 573 K (or 773 K) for 6 h. After cooling to room temperature, the sample was exposed to air. In the case of aqua regia treatment, the reduced sample was put into a mixture of HCl (12.1 N) and HNO_3 (15.9 N) (3:1 v/v), boiled on a water bath for 1 h, filtered and washed with hot water, and dried. The fact that most of Pt on external surface was removed by the aqua regia treatment was confirmed by a CO chemisorption method. In the case of photoreduction, a mixture of $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ powder (2 g), distilled water (290 ml) and methanol (10 ml) was irradiated by a high pressure mercury lamp (400 W) for 48 h in an inner irradiation type quartz reactor, then, it was filtered and washed with distilled water. On the other hand, H_2PtCl_6–$K_4Nb_6O_{17}$ was prepared by impregnation method.

Photocatalytic reaction was carried out in a closed gas-circulation system. A mixture of a catalyst (1 g), distilled water (350 ml) and a required amount of salt such as Na_2CO_3 or NaOH in an inner irradiation type quartz cell was deaerated completely by pumping away of gas phase time after time, and argon gas (35 Torr) was introduced into the system. The catalyst was suspended by stirring and irradiated by a high-pressure mercury lamp (400 W, Riko Kagaku). The evolution of H_2 and O_2 was analyzed by on-line gas chromatography (TCD, molecular sieve 5 A or active carbon, argon carrier gas) and by volumetric analysis with a pressure sensor.

Photographs of scanning electron microscopy (SEM) were obtained using an S-800 instrument (HITACHI) equipped with an energy dispersive X-ray spectroscopy (EDX, Kevex DELTA), and a sample was put on a carbon tape without gold adhesion. Photographs of transmission electron microscopy (TEM) were obtained using H-800S (HITACHI, 300 kV acceleration). Temperature programmed reduction (TPR) on reduction of $[Pt(NH_3)_4]^{2+}$/catalyst by H_2 was undertaken in a flow system, which was equipped with a conductance electrode immersed in dilute H_2SO_4 aqueous solution. Amount of NH_3 evolved from the sample was determined from the decrease of conductance of the solution. Increase rate of temperature in TPR measurement was 10 K/min. Amount of sample was 0.5 g and H_2 flow rate was 50 ml/min.

The extended X-ray absorption fine structure (EXAFS) spectroscopy of Pt L_{III}-edge (E_0 = 11,562 eV) were taken at Beam Line 10B (2.5 GeV, 200 mA, energy resolution was 1.5 eV) of Photon Factory in the National Laboratory for High Energy Physics (KEK-PF, Tsukuba, Japan). The synchrotron radiation was monochromatized by Si(311) channel-cut crystal. Total X-ray absorption coefficiency was adjusted to less than 3.0 and N_2 gas was used for 17 cm I_0 chamber and 34 cm I chamber to reduce the effects of higher harmonics to negligible level ($I_{333}/I_{111} < 10^{-4}$). $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ sample was washed well to remove excess $[Pt(NH_3)_4]Cl_2$. The sample was mixed with polyethylene homogeneously and was molded into a disk (2 cm diameter) to minimize heterogeneity of thickness. The EXAFS measurement was carried out in a transmission mode at room temperature in air. The method of curve-fitting analysis of EXAFS data has been described elsewhere [25]. Pt foil and $[Pt(NH_3)_4]Cl_2$ were used as standard samples for Pt–Pt and Pt–N bondings, respectively.

The amount of Pt in/on the catalyst in powder form was determined by X-ray fluorescence (XRF, SEIKO SEA-

2010). The amount of Pt on the external surface was estimated from the decrease of Pt after washing or aqua regia treatment.

FT-IR spectra of the catalyst in a diffuse reflectance mode were recorded by a BIO-RAD FTS-60 spectrometer with a resolution of 2 cm^{-1}. The IR cell could be evacuated and heated to remove water in the sample.

3. Results and discussion

3.1. Characterization of $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$

Fig. 1 shows SEM photographs of (a) Pt-intercalated $K_4Nb_6O_{17}$ ($Pt/K_4Nb_6O_{17}$) prepared from $[Pt(NH_3)_4]Cl_2$; (b) Pt-impregnated $K_4Nb_6O_{17}$ ($Pt-K_4Nb_6O_{17}$) prepared from H_2PtCl_6; and (c) Pt–$KNbO_3$ prepared from $[Pt(NH_3)_4]Cl_2$. All samples were reduced by H_2 at 573 K for 6 h, and the amount of Pt were ca. 2.5–3.0 wt.%. $KNbO_3$ is not a layered compound, and it has no ability to ion-exchange. The surface areas of $K_4Nb_6O_{17}$ and $KNbO_3$ were almost equal and were very small (BET surface areas were ca. 0.8 m^2/g). In the photographs (b) and (c), the heterogeneous aggregates of Pt particles which were like island (b) and cotton (c) could be observed. The Pt particle size was estimated at 10–50 nm from the SEM observation at high magnification. On the other hand, Pt particles could not be observed in the sample (a) by the SEM (resolution: <3 nm). The distribution of Pt particles in a large single crystal (ca. 1 mm) of the sample (a) was measured by EDX, and a difference in the Pt distribution between the center part and edge part of the layered crystal was not observed. Neither could Pt particles be observed by SEM on a sample of $Pt/K_4Nb_6O_{17}$ which had been photoreduced. We speculate that $[Pt(NH_3)_4]^{2+}$ cation could exchange with K^+ ion in the interlayer of $K_4Nb_6O_{17}$ homogeneously, but anionic $PtCl_6^{2-}$ could not because $K_4Nb_6O_{17}$ was cation-exchangeable material.

Fig. 2 shows TPR profiles of NH_3 desorption during H_2 reduction. The rate of NH_3 desorption was plotted as a function of the reduction temperature. The temperature at the peak of NH_3 desorption from $[Pt(NH_3)_4]Cl_2$, (a), was about 510 K. In the case of $[Pt(NH_3)_4]^{2+}$ ion-exchanged $K_4Nb_6O_{17}$ sample ($[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$) without washing by water after the ion-exchange, (b), two peaks at 520 K and 620 K were observed. Then, the first peak at 520 K became smaller by washing the sample (profile (c)). The peak temperature of $[Pt(NH_3)_4]Cl_2$–$KNbO_3$ was 520 K (profile (e)). Therefore, it was considered that the first peak at 520 K was the NH_3 desorption from the $[Pt(NH_3)_4]Cl_2$ on the external surface of $K_4Nb_6O_{17}$, and the second peak at 620 K was from the $[Pt(NH_3)_4]^{2+}$ in the interlayer. The Pt-complex on the external surface was easily removed by water washing, and it was easily decomposed by H_2 reduction. We infer from this finding that the $[Pt(NH_3)_4]^{2+}$ was remarkably stabilized against the H_2 reduction by its intercalation into the interlayer of $K_4Nb_6O_{17}$.

Both total amount of the desorbed NH_3 from the TPR samples up to 773 K and the amount of Pt in/on the sample measured by XRF were shown in Table 1. In the case of the $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ without washing, the amount of Pt and NH_3 in the sample increased proportionally with the concentration of the Pt-complex in the ion-exchange solution. The mole ratio of NH_3 to Pt in the samples before reduction was almost 4. About 90% of the Pt-complex in the solution was adsorbed in the $K_4Nb_6O_{17}$ in each cases. It was suggested that $[Pt(NH_3)_4]^{2+}$ was ion-exchanged into $K_4Nb_6O_{17}$ preferentially. Then, the amount of the external Pt-complex which could be removed by washing was estimated at ca. 10% of the total Pt-complex in/on the $K_4Nb_6O_{17}$. Furthermore, the amount of the external Pt which could be removed by the aqua regia treatment was ca. 16% of the total Pt in/on the sample after washing. As a result, more than 70% of the amount of Pt in the ion-exchange solution was present in the interlayer of $K_4Nb_6O_{17}$ even after the aqua regia treatment. The amount of Pt in the interlayer of the catalyst after H_2 reduction was almost the same as that after photoreduction. On the other hand, most of Pt on $K_4Nb_6O_{17}$ prepared from H_2PtCl_6 precursor were easily removed by aqua regia treatment.

Diffuse reflectance FT-IR spectra of $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ catalysts after several treatments and reference samples were shown in Fig. 3. All catalysts were washed well to remove the external Pt-complex. The IR absorptions of $[Pt(NH_3)_4]Cl_2$ (a) at 1337 cm^{-1} and 1580 cm^{-1} were assigned to symmetric and asymmetric NH bending, respectively, and the broad absorption at 3000–3400 cm^{-1} was assigned to NH stretching vibrations [26,27]. The observation of the symmetric NH bending was useful, because this peak was very sharp and strong, moreover the overlap with absorption of water was small. Though some IR absorption peaks were shifted toward the higher wavelength, the shapes of the spectra of $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ catalysts, ((b)–(d)), were similar to the spectrum of $[Pt(NH_3)_4]Cl_2$ (a), and they were different from the spectrum of $NH_4^+/K_4Nb_6O_{17}$ (e). Therefore, it is considered that the structure of $[Pt(NH_3)_4]^{2+}$ remained intact in the interlayer of $K_4Nb_6O_{17}$, and that some interactions between Pt-complex and niobium oxide sheets resulted in the IR peak shift. The symmetric NH bending of the $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ was observed at 1373 cm^{-1} under a medium-humid atmosphere, (b), under which only interlayer I was hydrated as $K_4Nb_6O_{17}\cdot 3H_2O$. Then, this peak was shifted to 1357 cm^{-1} under evacuation to remove all water in the interlayers, (c). These structures were confirmed by XRD measurement. The peak shift of the NH bending by hydration and/or dehydration of the interlayer I was reversible. The similar shift of the NH bending by hydration was also observed in $[Pt(NH_3)_4]^{2+}$-intercalated montmorillonite clay [17]. When the sample was exposed to a highly-humid atmosphere, (d), under which both interlayers I and II were hydrated as

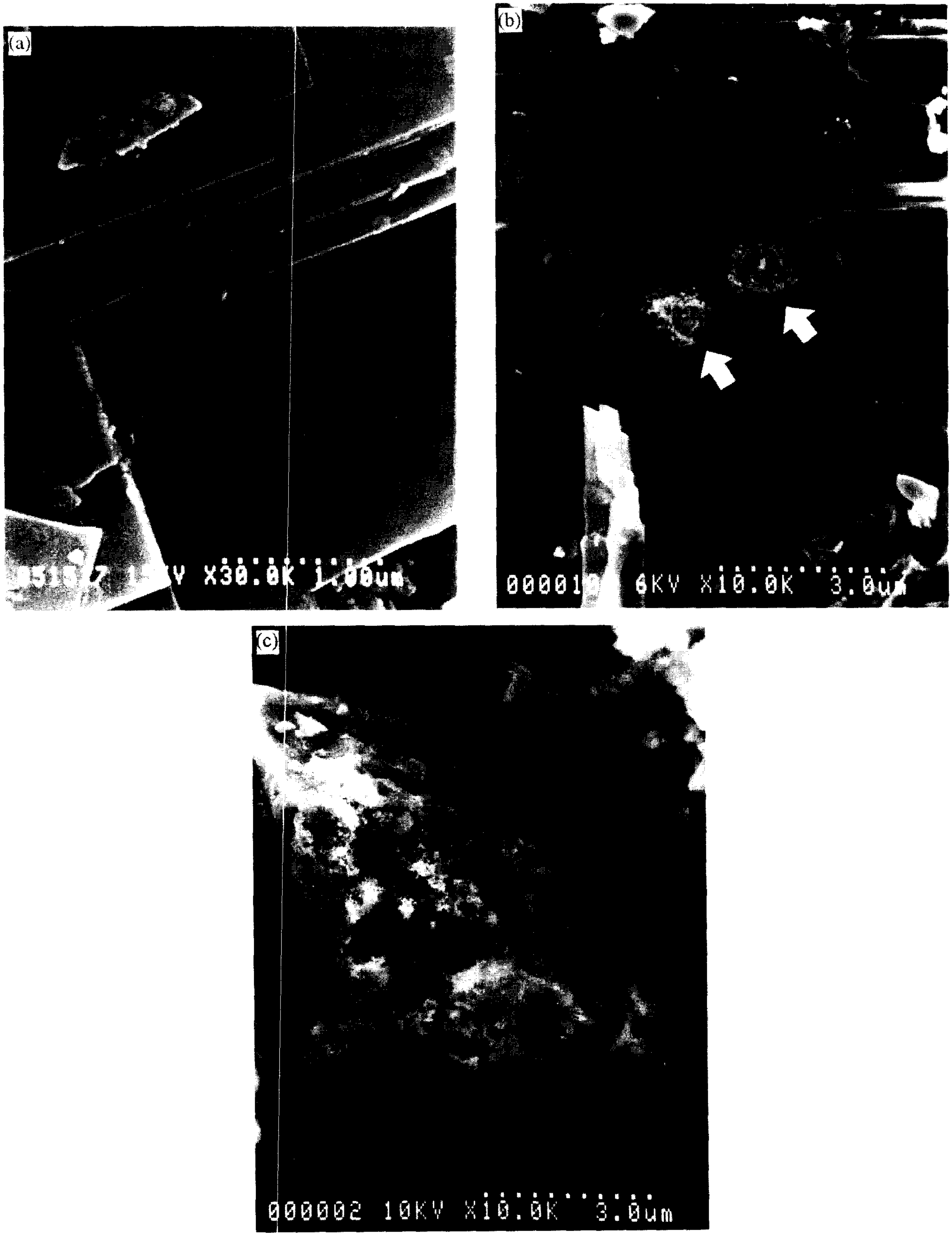

Fig. 1. SEM photographs of Pt loaded catalysts. (a) Pt-intercalated $K_4Nb_6O_{17}$ (Pt/$K_4Nb_6O_{17}$) prepared from $[Pt(NH_3)_4]Cl_2$; (b) Pt-impregnated $K_4Nb_6O_{17}$ (Pt–$K_4Nb_6O_{17}$) prepared from H_2PtCl_6; (c) Pt-$KNbO_3$ prepared from $[Pt(NH_3)_4]Cl_2$. All samples were reduced by H_2 at 573 K for 6 h, and amount of Pt were ca. 3 wt.%.

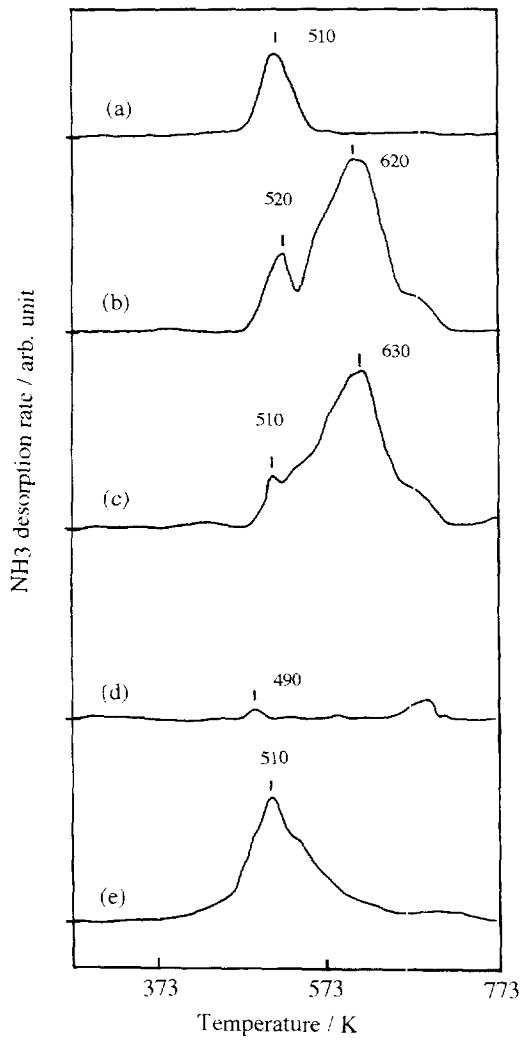

Fig. 2. TPR profiles on NH_3 desorption from $[Pt(NH_3)_4]^{2+}$/catalyst samples by H_2 reduction. (a) $[Pt(NH_3)_4]Cl_2$; (b) $[Pt(NH_3)_4]^{2+}$ ion-exchanged $K_4Nb_6O_{17}$ catalyst ($[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$) before washing; (c) $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ after washing; (d) $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ catalyst after H_2 reduction at 573 K for 6 h; (e) $[Pt(NH_3)_4]Cl_2$-loaded on $KNbO_3$.

$K_4Nb_6O_{17}\cdot nH_2O$ ($n > 5$), the NH bending was observed at 1377 cm^{-1}. The large peak shift compared to the peak of anhydride (1357 cm^{-1}) was observed under the condition that only interlayer I was hydrated (1373 cm^{-1}) as well as under the condition that both interlayers I and II were hydrated (1377 cm^{-1}). Therefore, it was concluded that $[Pt(NH_3)_4]^{2+}$ was located at least in the interlayer I. In the case of $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ sample reduced by H_2 at 573 K for 6 h (f), absorptions derived from $[Pt(NH_3)_4]^{2+}$ disappeared.

Fig. 4 and Table 2 show Fourier transforms of EXAFS spectra of Pt L_{III}, bonding length and coordination number. The EXAFS measurement was carried out in air, because catalysts were actually exposed to water and O_2 during photoreaction, and stable against water and O_2 for a long time. (a) $[Pt(NH_3)_4]Cl_2$ and (b) Pt foil were used as reference compounds. Peak 1 and peak 2 were represented by Pt–N bonding of amine complex salt ($R = 2.00$ Å, $N = 4$) and Pt–Pt bonding of Pt metal ($R = 2.77$ Å, $N = 12$), respectively. The spectrum of (c) $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ was very similar to the spectrum of $[Pt(NH_3)_4]Cl_2$, and the coordination number was estimated at 3.8 ± 0.5. Therefore, from the results of TPR, FT-IR and EXAFS, it was suggested that the coordination number of nitrogen to Pt atom and the structure of $[Pt(NH_3)_4]^{2+}$ were maintained in the interlayer of $K_4Nb_6O_{17}$. When the $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ was reduced by H_2 at 573 K for 6 h, (d), two large peaks were observed. The peak at 2.01 Å is likely due to Pt–O bonding, but not to Pt–N bonding, because the amount of NH_3 (and/or NH_4^+) in the catalyst after reduction was very small judging from the results of TPR and FT-IR. The peak at 2.63 Å might be Pt–Pt bonding, however, the observed bond length was 0.14 Å smaller than the Pt–Pt bond length found in the Pt metal standard (2.77 Å). When the $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ was reduced at 773 K, (e), Pt-complex was reduced to Pt metal, which was identified by curve fitting. The bonding length of Pt–Pt was 0.09 Å smaller than standard length of Pt metal, and coordination number was ca. 7.2 ± 1. In the case of the photoreduction (f), the Pt-complex was reduced to metal completely and coordination number was ca. 6.2 ± 1. The decrease of Pt–Pt bonding length was not observed. On the other hand, in both cases of the H_2PtCl_6 on $K_4Nb_6O_{17}$ (g) and the $[Pt(NH_3)_4]Cl_2$ on $KNbO_3$ (h), both coordination numbers were larger than that of spectra (e) and (f). It is suggested that these Pt precursors on outer surface of catalyst were easily reduced to large metal particles by H_2 reduction at 573 K, which was also shown in the results from SEM measurement.

The results of EXAFS as well as TPR show that the $[Pt(NH_3)_4]^{2+}$ complex was barely reduced in the interlayer spaces of $K_4Nb_6O_{17}$ compared with the external $[Pt(NH_3)_4]Cl_2$ complex. It was reported that $[Pt(NH_3)_4]^{2+}$ in montmorillonite which was the layered mineral was completely reduced by H_2 reduction at 413 K, and Pt migrated to the external surface [17]. The reason why the Pt complex was stabilized by intercalation into $K_4Nb_6O_{17}$ might be associated with the high charge density of the interlayer space and favorable packing. $K_4Nb_6O_{17}$ structure has very high charge density (0.08 Å^{-2}) compared to montmorillonite (0.017 Å^{-2}). When CO or H_2 chemisorption at room temperature was carried out over Pt (8 wt.%)/$K_4Nb_6O_{17}$ catalyst after H_2 reduction at 773 K and aqua regia treatment, it was found that neither CO nor H_2 could adsorb on/in the catalyst at all. The interlayer spaces of anhydrous $K_4Nb_6O_{17}$ were fully occupied by K^+ ion and they were very narrow because of strong ionic force between layers. Even the H_2 molecule hardly entered the interlayer spaces, therefore, a higher reduction temperature was required to reduce the Pt-complex within the interlayer space of $K_4Nb_6O_{17}$ than that on the external surface.

In order to measure the exact diameter of Pt particles in the interlayer spaces, the Pt/$K_4Nb_6O_{17}$ samples were observed by TEM as shown in Fig. 5. All samples were treated

Table 1
Amount of $[Pt(NH_3)_4]Cl_2$ to $K_4Nb_6O_{17}$ catalyst as Pt and NH_3 in the ion-exchange solution, and amount of Pt and NH_3 in/on the $K_4Nb_6O_{17}$ catalysts after several treatments

Amount in ion-exchange solution			Amount in/on the sample	
Pt (wt.% /g-cat)	NH_3 (μmol/g-cat)	Washing and treatment[a]	Pt[b] (wt.% /g-cat)	NH_3[c] (μmol/g-cat)
Pt (8 wt.%)	1640	No washing—no treatment	7.7	1570
		Washing—no treatment	7.4	1545
Pt (3 wt.%)	615	No washing—no treatment	2.8	579
		Washing—no treatment	2.5	561
		Washing—H_2 (573 K)	2.5	53
		Washing—H_2 (573 K)—AQ	2.1	20
		Washing—PHOTO	2.5	441
		Washing—PHOTO—AQ	2.1	–
Pt (1 wt.%)	205	No washing—no treatment	0.9	180
		Washing—no treatment	0.8	167
Pt (3 wt.%)[d]	–	No washing—H_2 (573 K)	2.9	–
	–	No washing—H_2 (573 K)—AQ	0.1	–

[a] Washing: sample was washed by pure water on a filter to remove Pt-complex on the outer surface, PHOTO: photoreduction in methanol solution for 48 h, H_2: H_2-reduction for 6 h, H_2 + AQ: H_2-reduction and aqua regia treatment.
[b] Amount of Pt in/on the sample was measured by XRF.
[c] Amount of NH_3 in the sample was measured by TPR up to 773 K.
[d] Pt precursor was H_2PtCl_6.

by aqua regia thoroughly. The Pt particles in the photoreduced sample, (a), were dispersed homogeneously and particle size was less than 6 Å. On the other hand, the dispersion of Pt particle in the H_2 reduced sample at 773 K, (b), was less homogeneous than that in the photoreduced sample. Most of particles were less than 5 Å in diameter, but some larger particles of greater than 15 Å could be observed in Fig. 5b.

The Pt particle size can be also estimated from the average coordination number in EXAFS measurement, assuming spherical particles of face-centered cubic (fcc) packing [28]. For the $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ reduced by H_2 at 773 K, the diameter of Pt particles was estimated to be 9–11 Å. In the case of the photoreduced catalyst, the diameter was estimated to be 8–10 Å. Though the structures of anhydrate and hydrate $K_4Nb_6O_{17}$ were analyzed in detail [5–7], estimation of the interlayer space width and layer thickness is difficult because the niobium layers are corrugated. When the layer thickness was assumed to be 4.1 Å, average space width of interlayers I and II of $K_4Nb_6O_{17}\cdot 3H_2O$ were estimated at 5.8 and 4.9 Å, respectively [8]. The interlayer space width at hollows between corrugated niobium oxide sheets might be wider than the average space width. However, the particle size estimated from EXAFS data is considerably larger that the interlayer space I. It means that some large Pt particles exist in those samples prepared without aqua regia treatment. The amount of Pt on the external surface of $K_4Nb_6O_{17}$ was estimated to be 16% of total Pt in the samples from the results of Table 1, and the size of external Pt particles might be larger than that of internal particle. The coordination numbers of the Pt particle in the sample (g) and (h) in Fig. 4 were ca. 10 as shown in Table 2. Therefore, in the case of the photoreduced sample, the coordination number of interlayer Pt particles was calculated at ca. 5.5 and the Pt diameter ca. 7 Å, provided that the coordination number of Pt on outer surface was assumed to be 10. This diameter value (7 Å) from the EXAFS measurement is close to the particle size from the TEM observation (6 Å) in the photoreduced sample. The interlayer space of $K_4Nb_6O_{17}$ during photoreduction was so enlarged flexibly by water that Pt particles of 7 Å could fit within the interlayer space. In the case of H_2 reduced sample, large Pt particles more than 15 Å were observed from the TEM observation. However, this larger Pt particle was too large to exist in the interlayer space. The larger Pt particles might have grown with destruction of the layered sheet.

The decrease of Pt–Pt bonding length was observed only in the H_2 reduced samples by EXAFS measurement. The decrease of Pt–Pt bonding length has been reported in several Pt loaded catalysts [20–22,29–33]. The following reasons for the decrease of bonding length were considered: asymmetric distribution of bonding length by thermal or static distortion effect [29–31], electron transfer effect from Pt metal to support [32], structure change into stable cluster by metal-support interaction or by small size effect [33], and so on. We carried out cumulant expansion analysis including 3-order and 4-order cumulants to avoid the effect of asymmetric distribution on bond length. But the results of bond length were not so much changed, that is, the shortening of Pt–Pt can not be explained only by asymmetric distribution. In the case of the H_2-reduced $Pt/K_4Nb_6O_{17}$, it was speculated that the main cause might be the pressure of the narrow interlayer space onto the Pt particles. When catalyst was reduced by H_2 more than 473 K, $K_4Nb_6O_{17}$ was anhydrate. The average space width of interlayer I of $K_4Nb_6O_{17}$ anhydrate was only 3.0 Å [8], and the interlayer spaces were fully occupied by K^+ ion. Therefore, it was easily imaged that the migration of Pt atom and the growth of Pt particles were significantly

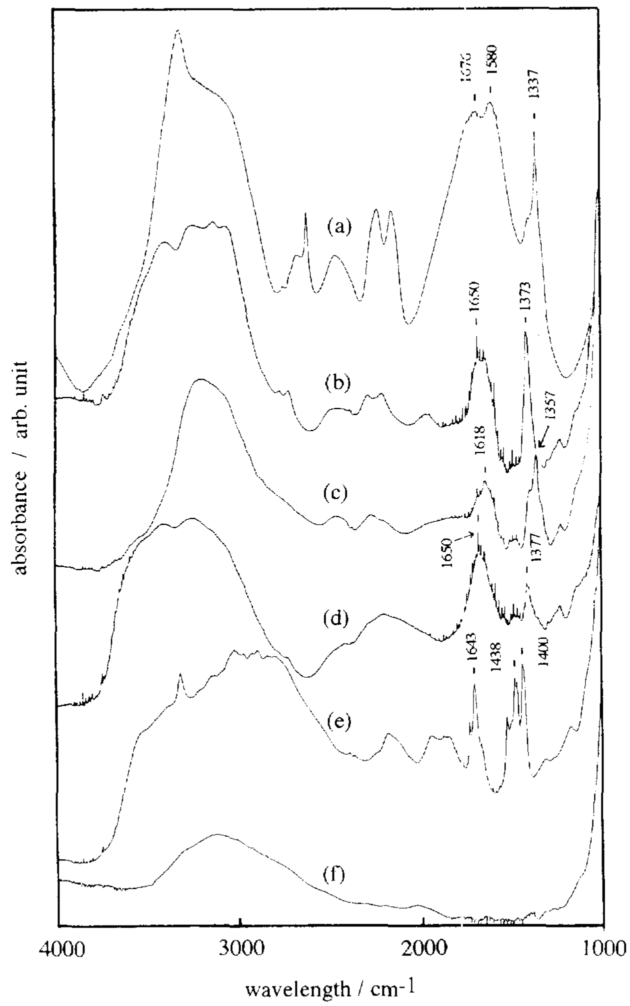

Fig. 3. Diffuse reflectance FT-IR spectra of $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ catalysts after several treatments and reference samples. (a) $[Pt(NH_3)_4]Cl_2$; (b) $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}\cdot 3H_2O$ under medium-humid atmosphere; (c) $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ anhydrate under evacuation; (d) $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}\cdot nH_2O$ ($n>5$) under high-humid atmosphere; (e) $NH_4^+/K_4Nb_6O_{17}$; (f) $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ sample reduced by H_2 at 573 K for 6 h. Amount of Pt were ca. 3 wt.%.

limited. On the other hand, the decrease of Pt–Pt bond length was not observed in the photoreduced sample, though very fine Pt particles were located in the interlayer space as same as the H_2 reduced sample. This is because Pt-complex was reduced in wide interlayer space broadened by water, and Pt atom could migrate freely.

3.2. Photocatalytic reaction over $Pt/K_4Nb_6O_{17}$

Table 3 shows the rate of H_2 and O_2 evolution over $Pt/K_4Nb_6O_{17}$ suspended in several solutions and irradiated with high-pressure Hg lamp. When $[Pt(NH_3)_4]Cl_2$ was used as a Pt-precursor and catalysts were suspended in pure water, NaOH, KOH, or Na_2SO_4 aqueous solution, little H_2 gas was detected and no O_2 gas was detected even after long irradiation time. On the other hand, the rate of gas evolution was increased very much by addition of Na_2CO_3 or K_2CO_3, and the near stoichiometric evolution of H_2 and O_2 (H_2:O_2 = 2:1) was observed. No evolution of CO_2 in gas phase was detected. The activity increased with the increase of carbonate concentration. The aqua regia treatment was not necessary to show the stoichiometric water splitting when carbonate solution was used. The pH of Na_2CO_3 aqueous solution was ca. 11. Some reactions in phosphate buffer solutions of pH = 11 were tested, however, the water splitting reaction did not take place. With regard to the reduction method of the catalyst, the photoreduction was superior to the H_2 reduction for preparation of $Pt/K_4Nb_6O_{17}$ catalyst. Actually, the activity of the catalyst prepared by photoreduction was larger than that of the sample prepared by H_2 reduction. The activity of the H_2-reduced catalyst decreased with the reduction temperature. This may have occurred because photoreduction under mild conditions might have fully reduced the Pt-complex without damage to the layered structure, while high temperature H_2 reduction might have gradually destroyed the layered structure.

In order to decompose water effectively, either the aqua regia treatment or the carbonate addition was essential for $Pt/K_4Nb_6O_{17}$ photocatalyst. A further enhancement of the promotion effect was expected by combination of the aqua regia treatment and the carbonate addition method, however, cooperative promotion effect was not observed as shown in Table 3. We speculate that the catalyst might be injured by aqua regia treatment, because repetition of the treatment caused deactivation of the catalysts actually. When H_2PtCl_6 was used as a precursor, both H_2 and O_2 gases were evolved from Na_2CO_3 solution, but the activity was very small compared to the catalysts prepared from $[Pt(NH_3)_4]Cl_2$.

Time course of H_2 and O_2 evolution over Pt (0.3 wt.%)/$K_4Nb_6O_{17}$ catalyst prepared from $[Pt(NH_3)_4]Cl_2$ is shown in Fig. 6. When the catalyst treated with aqua regia was suspended in pure water, (a), the rate of gas evolutions gradually decreased with reaction time. Because the internal Pt particle might be exposed to outside by cleavage of the layered catalyst during reaction, and rapid backward reaction ($2H_2 + O_2 \rightarrow 2H_2O$) might occur on the external Pt. On the other hand, when the catalyst was suspended in Na_2CO_3 aqueous solution, (b), the rate of gas evolution was constant after 10 h from the start of irradiation, and decay of the activity with time was not observed up to 200 h. Total amount of evolved H_2 and O_2 for 200 h were ca. 90 mmol and 45 mmol, respectively.

Fig. 7 shows the dependence of the activity on the amount of Pt. All catalysts were suspended in a concentrated Na_2CO_3 solution and they were not treated with aqua regia. The activity of $Pt/K_4Nb_6O_{17}$ prepared from $[Pt(NH_3)_4]Cl_2$ increased with the amount of loaded Pt. The maximum activity was obtained over Pt (5 wt.%)/$K_4Nb_6O_{17}$ catalyst, and it was 1.04 mmol/h (23.3 ml/h) of H_2 evolution and 0.52 mmol/h (11.6 ml/h) of O_2 evolution, respectively. This gas evolution rate was very high compared to other catalyst systems, however, quantum efficiency in this system was not decided yet.

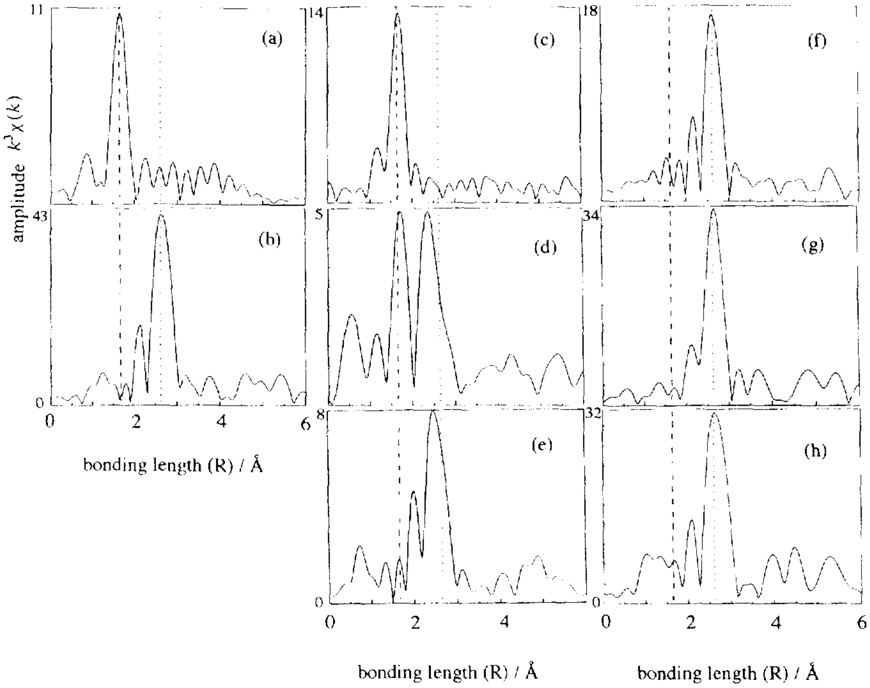

Fig. 4. Fourier transforms of Pt L_{III} edge EXAFS functions $K^3X(K)$ of $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$ catalysts and references. Amount of Pt in the samples were ca. 3 wt.%. Phase shift was not corrected. (a) $[Pt(NH_3)_4]Cl_2$; (b) Pt foil; (c) untreated catalyst; (d) reduced catalyst by H_2 at 573 K for 6 h; (e) reduced catalyst by H_2 at 773 K for 6 h; (f) photoreduced catalyst in methanol aqueous solution for 48 h; (g) Pt–$K_4Nb_6O_{17}$ prepared from H_2PtCl_6 precursor by H_2 at 573 K for 6 h; (h) $PtKNbO_3$ prepared from $[Pt(NH_3)_4]Cl_2$ precursor by H_2 at 573 K for 6 h. Peak 1 (- - -) and peak 2 (· · ·) correspond to standard Pt–N and Pt–Pt bonding length, respectively.

Table 2
Pt L_{III} edge EXAFS data of several Pt loaded catalysts

Catalyst	Pre-treatment[a]	Pt–N (or Pt–O)		Pt–Pt	
		R (Å)[b]	*N*[c]	*R* (Å)[b]	*N*[c]
(a) $[Pt(NH_3)_4]Cl_2$[d]		2.00	4.0		
(b) Pt foil[d]				2.77	12
PtO_2[d]		2.00			
(c) $[Pt(NH_3)_4]^{2+}/K_4Nb_6O_{17}$	Untreated	2.02 ± 0.02	3.8 ± 0.5		
(d)	H_2 (573 K)	2.01 ± 0.02	(1.2 ± 2)	2.63 ± 0.02	(2.6 ± 2)
(e)	H_2 (773 K)			2.68 ± 0.02	7.2 ± 1
(f)	PHOTO			2.77 ± 0.02	6.2 ± 1
(g) $H_2PtCl_6 + K_4Nb_6O_{17}$	H_2 (573 K)			2.77 ± 0.02	9.8 ± 1
(h) $[Pt(NH_3)_4]^{2+} + KNbO_3$	H_2 (573 K)			2.76 ± 0.02	10.2 ± 1

[a] PHOTO: photoreduction in methanol solution for 48 h. Without aqua regia treatment. H_2: H_2-reduction for 6 h. Without aqua regia treatment.
[b] *R*: interatomic distance between an absorber Pt atom and a scatterer atom.
[c] *N*: average coordination number of the sphere.
[d] Standard sample for references.

3.3. Reaction mechanism of $Pt/K_4Nb_6O_{17}$

Platinum metal is known as an excellent electrode material for H_2 evolution because of its extremely low overpotential for H_2 evolution. The activity of Pt-intercalated catalysts increased monotonously with the amount of Pt up to 5 wt.% as shown in Fig. 7. The activity of Pt-intercalated $K_4Nb_6O_{17}$ prepared from $[Pt(NH_3)_4]Cl_2$, (a), was much higher than that of Pt-loaded $K_4Nb_6O_{17}$ prepared from H_2PtCl_6, (b), in all Pt-amount region. Therefore, it is almost certain that Pt is the H_2 evolution site, and that most of the H_2 evolution reaction takes place on Pt particles in the interlayer spaces and the H_2 evolution on Pt at the external surface of $K_4Nb_6O_{17}$ is negligible.

$K_4Nb_6O_{17}$ has two different kinds of interlayer spaces. Which interlayer was the Pt particles located in? Kinomura et al. [8] reported that K^+ ions in interlayer II were substituted by only monovalent cations whereas K^+ ions in interlayer I were substituted by both mono- and bivalent cations such as Ni^{2+} and Ca^{2+}. Moreover, the maximum percentage of ion-exchangeable K^+ ions of the $K_4Nb_6O_{17}$ in highly-concentrated $[Pt(NH_3)_4]Cl_2$ solution was less than 50%.

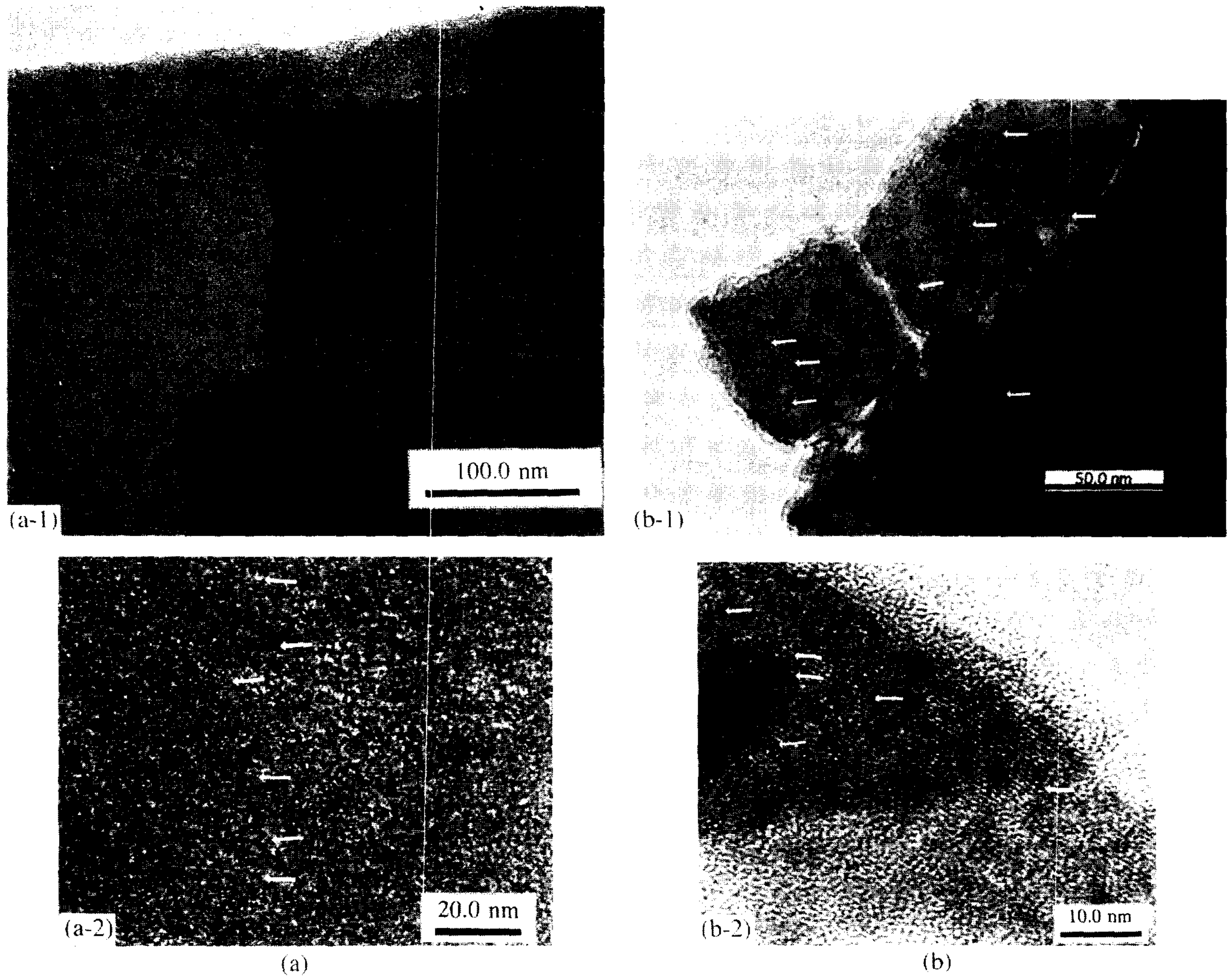

Fig. 5. TEM photographs of Pt (3 wt.%)/$K_4Nb_6O_{17}$ catalysts. (a-1) and (a-2) Low and high magnification of photoreduced catalyst, respectively. $[Pt(NH_3)_4]^{2+}$/$K_4Nb_6O_{17}$ was photoreduced in methanol aqueous solution for 48 h. (b-1) and (b-2) Low and high magnification of H_2 reduced catalyst, respectively. $[Pt(NH_3)_4]^{2+}$/$K_4Nb_6O_{17}$ was reduced by H_2 at 773 K for 6 h.

From the results of the FT-IR measurement, it was concluded that $[Pt(NH_3)_4]^{2+}$ ions were located at least in the interlayer I. Therefore, it seems reasonable to assume that most of $[Pt(NH_3)_4]^{2+}$ bivalent cations are considered to intercalate only into interlayer I preferentially, and fine Pt metal particles might exist only in interlayer I after H_2- or photoreduction.

From the results discussed above, it is probable that most of the O_2 evolution occurred in interlayer II: Plane size of the layered catalyst was 1–10 μm, and it was suggested from TEM and EDX data that Pt was dispersed in the catalyst uniformly. In the case of Pt (10 wt.%)/$K_4Nb_6O_{17}$, more than 20% of K^+ in the interlayer I were replaced by $[Pt(NH_3)_4]^{2+}$, and it showed good activity despite the presence of much amount of Pt which could carry out the thermal back reaction between H_2 and O_2. If both H_2 and O_2 gases evolved in the same interlayer I, the backward reaction to form H_2O must take place instantly. Therefore, the O_2 evolution might occur in the interlayer II which was isolated from H_2 evolution site. When the catalyst was irradiated by UV light, electrons and holes were generated in the niobium oxide sheet. The chemical properties of interlayers I and II were very different, and the differences may provide a driving force for charge separation of electrons and holes in the sheet. In the reaction mechanism as shown in Fig. 8, H_2 and O_2 gases are not mixed with each other in the interlayer spaces due to separation by the niobium oxide sheet, therefore, the backward reaction on the internal Pt might be negligible.

In the case of several Pt-loaded photocatalysts such as Pt–TiO_2 [11,12], Pt/$K_4Nb_6O_{17}$, Pt–$K_2Ti_6O_{13}$ [14] and so on, the addition of carbonate or bicarbonate salts was essential for water splitting. It is certain that CO_3^{2-} or HCO_3^- anions played the excellent role for this reaction. Several kinds of effects of carbonates were considered over these Pt-loaded catalysts [11–16]; suppression effect of the back recombination reaction ($2H_2 + O_2 \rightarrow 2H_2O$) on Pt, acceleration of the charge separation by hole trapping over the surface carbonate anions, O_2 formation via peroxocarbonate intermediates, and so on. However, Pt-intercalated $K_4Nb_6O_{17}$ is very different from the Pt-loaded catalysts. The carbonate anions can not directly affect the interlayers which are the reaction sites of

Table 3
Rate of H_2 and O_2 evolution over several Pt (0.3 wt.%)-$K_4Nb_6O_{17}$ catalysts

Pt-precursor	Reaction solution (mol/l)	Reduction method[a] (K)	Rate of gas evolution[b] (μmol/h)	
			H_2	O_2
$[Pt(NH_3)_4]Cl_2$	Pure water	PHOTO	1	0
	NaOH (1.1)	PHOTO	2	0
	KOH (1.1)	PHOTO	1	0
	Na_2SO_4 (1.1)	PHOTO	1	0
	Na_3PO_4 (0.1) + Na_2HPO_4 (0.5)	PHOTO	2	0
	Na_2CO_3 (0.3)	PHOTO	20	7
	Na_2CO_3 (1.1)	PHOTO	124	60
	Na_2CO_3 (2.2)	PHOTO	451	217
	K_2CO_3 (2.2)	PHOTO	274	130
	Na_2CO_3 (2.2)	H_2 (573 K)	293	123
	Na_2CO_3 (2.2)	H_2 (773 K)	230	110
	Pure water	H_2 (573 K) + AQ	31[c]	13[c]
	Na_2CO_3 (2.2)	H_2 (573 K) + AQ	214	101
H_2PtCl_6	Pure water	PHOTO	1	0
	Na_2CO_3 (2.2)	PHOTO	12	2
	Na_2CO_3 (2.2)	H_2 (573 K)	10	1

Catalyst: 1.0 g, Pt: 0.3 wt.%, water: 350 ml, an inner irradiated type quartz cell, high pressure Hg lamp (400 W).

[a] PHOTO: photoreduction for 48 h; H_2: H_2-reduction for 6 h; H_2 + AQ: H_2-reduction and aqua regia treatment.

[b] Activity was measured after 24 h from the start of irradiation.

[c] Amount of Pt was 0.01 wt.%, which was the optimum amount under the condition [10].

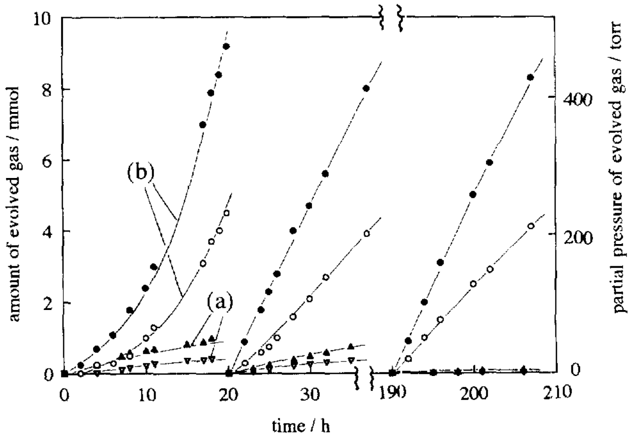

Fig. 6. Time courses of H_2 and O_2 evolution over Pt (0.3 wt.%) / $K_4Nb_6O_{17}$ catalysts. Catalysts were prepared from $[Pt(NH_3)_4]Cl_2$ by photoreduction. After every 18-h irradiation, the evolved gases were pumped away. (a) Catalysts was treated with aqua regia and it was reacted in pure water (H_2: ▲, O_2: ▽). (b) Catalyst was not treated with aqua regia, and it was reacted in Na_2CO_3 aqueous solution (2.2 mol/l) (H_2: ●, O_2: ○).

Pt/$K_4Nb_6O_{17}$, because anions can not enter the interlayer spaces by electric repulsion. Therefore, we infer that carbonate anions might affect secondary reactions, namely the back recombination reaction between H_2 and O_2 over Pt particles on the external surface. The complete suppression effect of the back reaction over Pt is required for the occurrence of the stoichiometric H_2 and O_2 evolution, and it has proved to be one of the important roles of carbonate salts addition from the results of studies on Pt–TiO_2 [11,12] and Pt–ZrO_2 [15,16] catalysts, therefore, similar suppression mechanisms of the back reaction were also considered on the Pt/$K_4Nb_6O_{17}$ catalyst. There was observed on induction period of 10 h from the start of irradiation as shown in Fig. 6. The external surface of catalyst might be modified by interaction with

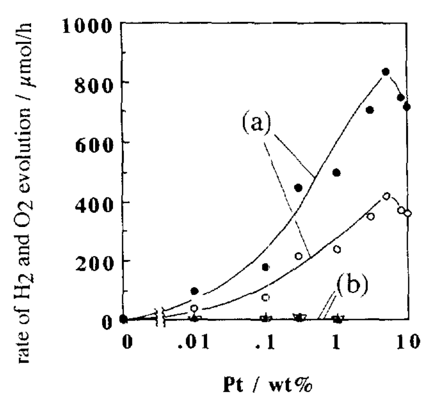

Fig. 7. Dependence of the activity over Pt/$K_4Nb_6O_{17}$ catalysts upon the amount of Pt. Catalysts were suspended in Na_2CO_3 solution and they were not treated with aqua regia. (a) Pt/$K_4Nb_6O_{17}$ prepared from $[Pt(NH_3)_4]Cl_2$ precursor (H_2: ●, O_2: ○); (b) Pt–$K_4Nb_6O_{17}$ prepared from H_2PtCl_6 precursor (H_2: ▲, O_2: ▽).

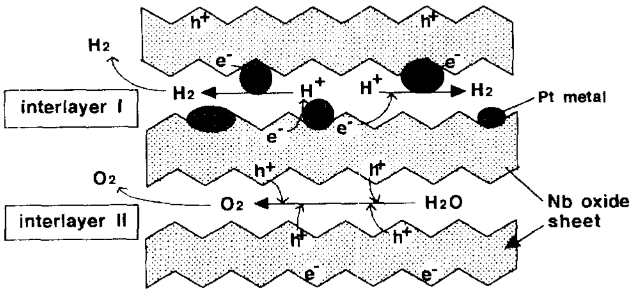

Fig. 8. Schematic structure of the Pt/$K_4Nb_6O_{17}$ photocatalyst and the reaction mechanism of H_2O decomposition into H_2 and O_2.

carbonate anions during the induction period. A decay of the gas evolution rate was not observed over Pt/$K_4Nb_6O_{17}$ suspended in Na_2CO_3 solution, probably because the external Pt particles were modified by carbonate even if the internal Pt particles were exposed to outside due to disruption of the layered catalyst.

4. Conclusions

In this study, both the behavior of Pt-complex in the layered compound on the reduction process and the structure of Pt/$K_4Nb_6O_{17}$ as well as the photocatalytic behavior of it were examined. Main conclusions are summarized as follows.

(1) The $[Pt(NH_3)_4]^{2+}$ cation was preferentially intercalated into the interlayer I of $K_4Nb_6O_{17}$.

(2) The $[Pt(NH_3)_4]^{2+}$ was stabilized by the intercalation toward reduction by H_2. More than 100 K higher temperature was required to reduce the $[Pt(NH_3)_4]^{2+}$ in the interlayer compared to that on the outer surface of the catalyst. It was considered that neutral H_2 molecule could barely come into contact with the $[Pt(NH_3)_4]^{2+}$ in the interlayer which have strong charge density and favorable packing.

(3) In the case of the H_2 reduction at 773 K, larger particles more than 15 Å was also observed by TEM. The decrease of Pt–Pt bond length was observed, and it was speculated that the growth of Pt particle was limited in the narrow interlayer space during the H_2 reduction.

(4) In the case of the photoreduction, fine Pt metal particles less than 6 Å could be prepared homogeneously in the interlayer space in a mild condition. The photocatalytic activity for the water decomposition over the Pt/$K_4Nb_6O_{17}$ prepared by the photoreduction was higher than that by the H_2 reduction.

(5) The photocatalytic water decomposition could easily proceed by the addition of carbonate salt in spite of the exposure of Pt particles on the outer surface of catalyst, therefore, the treatment of aqua regia was not essential in the presence of carbonates. Furthermore, deactivation of the catalyst was not observed for long time. It was considered that the carbonate ion might have a excellent roll for suppression of the backward reaction ($2H_2+O_2\rightarrow 2H_2O$) on the external Pt particles effectively.

(6) From all results, it seems reasonable to assume that the Pt particles in the interlayer I acted as H_2 evolution site, and that the O_2 evolution might occur in the interlayer II which was isolate from H_2 evolution site.

References

[1] K. Domen, A. Kudo, A. Shinozaki, A. Tanaka K. Maruya, T. Onishi, J. Chem. Soc., Chem. Commun. (1986) 356.
[2] A. Kudo, K. Domen, A. Tanaka, K. Maruya, K. Aika, T. Onishi, J. Catal. 111 (1988) 67.
[3] K. Sayama, A. Tanaka, K. Domen, K. Maruya, T. Onishi, Catal. Lett. 4 (1990) 217.
[4] K. Sayama, A. Tanaka, K. Domen, K. Maruya, T. Onishi, J. Catal. 124 (1990) 541.
[5] M. Gasperin, M.T. Le Bihan, J. Solid State Chem. 33 (1980) 83.
[6] M. Gasperin, M.T. Le Bihan, J. Solid State Chem. 43 (1982) 346.
[7] G. Legaly, K. Beneke, Inorg. Nucl. Chem. 38 (1976) 1513.
[8] N. Kinomura, N. Kumada, F. Muto, J. Chem. Soc., Dalton Trans. (1985) 2349.
[9] A. Kudo, K. Sayama, A. Tanaka, K. Asakura, K. Domen, K. Maruya, T. Onishi, J. Catal. 120 (1989) 337.
[10] K. Sayama, A. Tanaka, K. Domen, K. Maruya, T. Onishi, J. Phys. Chem. 95 (1991) 1345.
[11] K. Sayama, H. Arakawa, J. Chem. Comun. (1992) 150.
[12] K. Sayama, H. Arakawa, J. Chem. Soc., Faraday Trans. 93 (1997) 1647.
[13] K. Sayama, H. Arakawa, Chem. Lett. (1992) 253.
[14] K. Sayama, H. Arakawa, J. Photochem. Photobiol. A Chem. 77 (1994) 243.
[15] K. Sayama, H. Arakawa, J. Phys. Chem. 97 (1993) 531.
[16] K. Sayama, H. Arakawa, J. Photochem. Photobiol. A Chem. 94 (1996) 67.
[17] J.B. Harrison, V.E. Berkheiser, G.W. Erdos, J. Catal. 112 (1988) 126.
[18] M.G. Samant, M. Boudart, J. Phys. Chem. 95 (1991) 4070.
[19] M.S. Tzou, B.K. Teo, W.M.H. Sachtler, J. Catal. 113 (1988) 220.
[20] J.T. Miller, B.L. Meyers, F.S. Modica, G.S. Lane, M. Vaarkamp, D.C. Koningsberger, J. Catal. 143 (1993) 395.
[21] M. Vaarkamp, F.S. Modica, J.T. Miller, D.C. Koningsberger, J. Catal. 144 (1993) 611.
[22] F.W.H. Kampers, C.W.R. Engelen, J.H.C. van Hooff, D.C. Koningsberger, J. Phys. Chem. 94 (1990) 8574.
[23] C. Besoukhanova, J. Guidot, D. Barhomeuf, J. Chem. Soc., Faraday Trans. I 77 (1981) 1595.
[24] O.V. Bargin, E.S. Shpiro, A.V. Preobrazhensky, S.A. Isaev, T.V. Vasina, B.B. Dyusenbina, G.V. Antoshin, K.M. Minachev, Appl. Catal. 27 (1986) 219.
[25] N. Kosugi, H. Kuroda, EXAFS analysis Program, EXAFS2, Research Center for Spectrochemistry, University of Tokyo.
[26] J. Hiraishi, I. Nakagawa, T. Shimanouchi, Spectrochim. Acta A 24 (1968) 819.
[27] H. Poulet, P. Delorme, J.P. Mathiev, Spectrochim. Acta 20 (1964) 1855.
[28] R. Greegor, F. Lytle, J. Catal. 63 (1980) 476.
[29] R.W. Joyner, J. Chem. Soc., Faraday Trans. I 76 (1980) 357.
[30] E.C. Marques, D.R. Sandstrom, F.W. Lytle, R.B. Greegor, J. Chem. Phys. 77 (1982) 1027.
[31] E.S. Shpiro, R.W. Joyner, K.M. Minachiev, D.A. Pudner, J. Catal. 127 (1991) 366.
[32] T. Fukushima, J.R. Katzer, D.T. Sayers, J. Cook, Proc. Int. Catal. Congr., 7th, Tokyo, 1980.
[33] B. Moraweck, A.J. Renouprez, Surf. Sci. 106 (1981) 35.