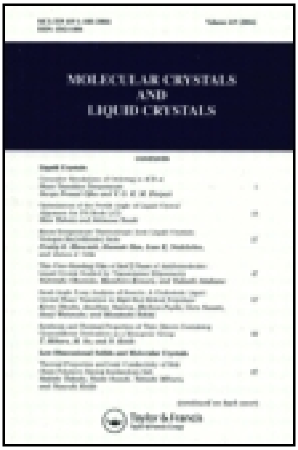

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Intercalation and Pillaring of Layered Tantalate Photocatalysts

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Version of record first published: 27 Oct 2006

To cite this article: Masato Machida, Jun-Ichi Yabunaka & Tsuyoshi Kijima (2000): Intercalation and Pillaring of Layered Tantalate Photocatalysts, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 249-252

To link to this article: http://dx.doi.org/10.1080/10587250008026148

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 249-252
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Intercalation and Pillaring of Layered Tantalate Photocatalysts

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(In final form June 25, 1999)

The layered tantalate photocatalysts ($MLnTa_2O_7$, M=Rb,Na,H) showed the structure-sensitive activity for H_2 evolution from aqueous methanol solution, which was the highest for the protonated phase but very low after SiO_2-pillaring through stepwise exchange processes.

Keywords: layered tantalate; photocatalyst; pillared structure

INTRODUCTION

The synthesis of pillared structures from layered titanates or niobates has led to the development of a new class of porous nanocomposite materials, which can be used as photocatalysts.[1-5] Their preparation is generally based on stepwise exchange of interlayer cations, including protonation, intercalation of alkylamines, and subsequent incorporation of pillaring agents, which are converted to oxide pillars upon heating. The resulting microporous structure is characterized by interlayer spaces with 1-2 nm wide, high specific surface areas (50-300 m^2/g), and a wide variety of possible chemical combinations between layers and pillars. The catalytic properties of layered hosts based on various transition metal oxides are expected to lead to a novel family of functional pillared solids. We describe here the first example of pillaring of the tantalates with layered perovskite-type structure, which was developed by Sato et al.[6], together with their photocatalytic property for hydrogen evolution reactions.

EXPERIMENTAL

The layered tantalate ($RbLnTa_2O_7$, Ln=rare earth) was obtained by calcination of oxides and caronate (Rare metallic, Co. Ltd.) at 1100 °C and subsequently submitted to ion exchange in molten $NaNO_3$ at 400 °C to convert into Na-type.[6] The product was then protonated in 1M HCl for 1 week. The following stepwise reactions with an aqueous solutions of 5M $C_6H_{13}NH_2$ and $C_{10}H_{21}NH_2$ were carried out at room temperature for 3 days, respectively. The resultant solids were treated in 3-aminopropyl triethoxysilane (APS) for 3 days with stirring. The pillared materials were obtained by calcination at elevated temperatures (300-500 °C) in an O_2 stream. The photocatalytic H_2 evolution from mixtures of powder samples (0.2 g) and an aqueous solution of 4M MeOH (200 cm^3)was took place in a Pyrex cell connected to a gas circulation system under photoirradiation from a 400W high-pressure Hg lamp.[4,5]

RESULTS AND DISCUSSION

The formation of single phase layered perovskite was obtained for Ln=La, Pr, Nd, and Sm, depending on the ionic radius of Ln^{3+}, which is required to be larger than 0.126 nm. As shown in Fig.1 the crystal structure is characterized as a two-dimensional framework comprised of two corner-shared TaO_6 octahedra and Rb ions in the interlayer. Figure 2a shows the change of XRD patterns in the pillaring process of $RbLaTa_2O_7$. Ion exchange resulted in the replacement of ca.90% of Rb^+ by Na^+ and then by H^+. After protonation a shift of the (002) reflection suggested the decrease of interlayer distance from

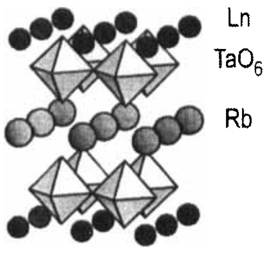

FIGURE 1 Crystal structure of layered tantalate ($RbLnTa_2O_7$).

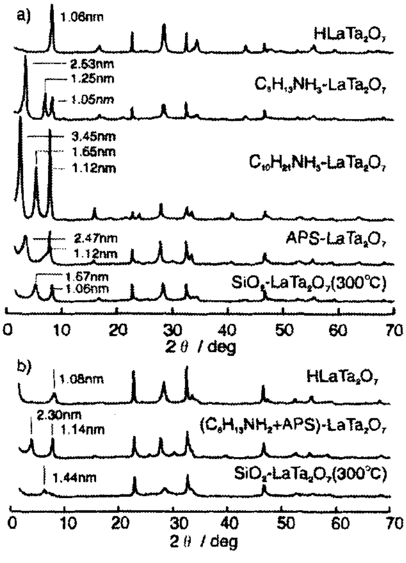

FIGURE 2 XRD patterns of layered tantalate in a) stepwise exchange process and b) direct reaction with hexylamine/APS mixtures.

1.23 to 1.06 nm. This is consistent with a fact that the Na-type sample was a hydrous compound corresponding to the composition of $NaLaTa_2O_7 \cdot 1.53H_2O$, whereas the protonated sample was composed of almost anhydrous interlayers. The hexylamine- and decylamine-intercalated tantalates showed much expanded interlayer distance, 2.59 and 3.45 nm, respectively. These values imply the formation of double layer of these amines in the interlayer. Further treatment with APS produced an intercalation compound (Si/Ta=1.77) with the interlayer distance of 2.47 nm, which decreased to 1.67 nm after calcination at 400 °C in air. However, the BET surface area of this SiO_2-pillared tantalate was only 5.6 m^2/g. We have also examined the reaction of the protonated phase with $C_6H_{13}NH_2$/APS mixtures as shown in Fig. 2b. The calcined product in this case showed the interlayer distance of 1.44 nm and surface area of 15.8 m^2/g. A possible reason for this low surface area as compared to those of other pillared samples is the nonporous structure in which SiO_2 stuffed the interlayer.

Figure 3 shows the UV-vis reflectance spectra of layered tantalates. The absorption onset of $RbLaTa_2O_7$ was little changed by exchange and pillaring. The corresponding band gap energy was about 3.8 eV, which was larger than those of Ta_2O_5(3.7eV) and layered titanates (3.1-3.6eV). The pillared sample showed the continuous absorption in the visible light region due to the carboneous deposits in the nonporous structure. Figure 4 shows the rate of H_2 evolution from 4M methanol solution over layered tantalates with different types of interlayer species before and after photodeposition of Pt. The protonated sample showed the higher activity as compared to the Rb- and Na-types and Ta_2O_5. A similar effect of protonation was also observed on the photocatalytic activities of layered tri- and tetratitanates ($Na_2Ti_3O_7$, $K_2Ti_4O_9$) in our previous study.[4,5] A further increase of the activity was attained after deposition of 0.1-1 mass% Pt onto the tantalate sample. For 0.1mass%Pt/$HLaTa_2O_7$, the initial activity was retained after 1200 min of irradiation and the total amount of H_2 evolved was 8 mmol, being exceedingly larger than the nominal amount of tantalates. This indicates that the H_2 evolution in this case proceeds catalytically. Interestingly, however,

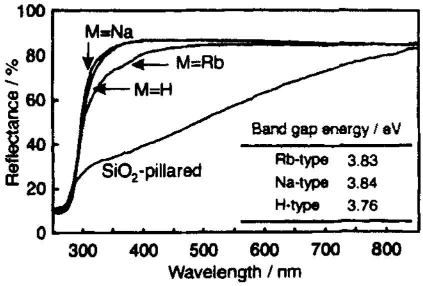

FIGURE 3 UV-vis reflectance spectra and band gap energy of $MLaTa_2O_7$.

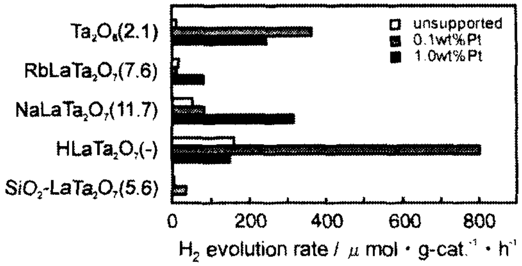

FIGURE 4 The photocatalytic activity of layered tantalate for H_2 evolution from aqueous MeOH solution. The values in parentheses show BET surface area (m^2/g) of tantalates.

the activity of the SiO_2-pillared tantalates was very low even after the Pt deposition. This is in complete contrast to the case of porous pillared layered titanates, of which activity was superior to that of unpillared samples.[4,5] Since the surface of the tantalate was unlikely covered by inert SiO_2 layer as detected by XPS, the deactivation caused by pillaring appears to be associated with the stuffed interlayer structure. This implies that the structure and chemical species in the interlayer space play a key role in photocatalysis of layered tantalates.

Acknowledgment

The one of authors (M.M.) thanks Tokuyama Science Foundation for the financial support of this study.

References

[1] J. Kondo, S. Shibata, Y. Ebina, K. Domen and A. Tanaka, *J. Phys. Chem.*, **99**, 1604 (1995).
[2] S. Uchida, Y. Yamamoto, Y. Fujishiro, A. Watanabe, O. Ito, and T. Sato, *J. Chem. So Faraday Trans.*, **93**, 3229 (1997).
[3] W. Shagguan, K. Inoue and A. Yoshida, *J. Chem. Soc. Chem. Commun.*, 779 (1998).
[4] M. Machida, J. Yabunaka, H. Taniguchi, and T. Kijima, *in Preparation of Catalys VII*, Elsevier, Amsterdam, 1998, p.951.
[5] M. Machida, X.Y. Ma, H. Taniguchi, J. Yabunaka, and T. Kijima, *J. Mol. Catal.*,, i press.
[6] K. Toda, K. Uematsu and M. Sato, *J. Ceram. Soc. Jpn.*, **105**, 482 (1997).