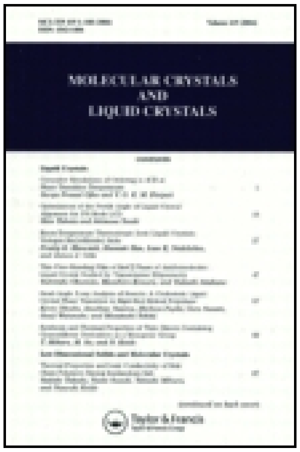

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Photocatalytic Production of Hydrogen on Reduced CrO_3-Graphite Intercalation Compound

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Abstract A photocatalyst for the production of hydrogen due to UV-illumination of water was prepared by the reduction of CrO_3-graphite intercalation compound (CrO_3-GIC) in K-naphtalenide/anhydrous THF solution. The creation of active sites on the catalyst surface was estimated during the activity measurements performed in dynamic conditions. The EDX analysis revealed an exact coincidence of the distribution lines for chromium and potassium in the whole of graphite flakes of the CrO_3-GIC/K photocatalyst.

Keywords: CrO_3-GIC-based catalyst; photocatalytic decomposition of water; production of hydrogen

INTRODUCTION

In recent years the photocatalytic decomposition of water has received much attention. This process is of particular interest due to its ability to utilise the solar energy. The photodecomposition of water has been mostly studied on semiconductors working due to the electron-hole process activated by the light absorption. Many n-type semiconductors, such as titanium dioxide, in water suspension, induce catalytic water decomposition under light illumination with the energy higher than the bandgap of the semiconductor. Recently the materials with a layered perovskite structure have been suggested to work as 'two-dimensional' photocatalysts in which catalytic reactions proceed at the interlayer spaces of catalyst[1,2]. Photocatalytic behaviour has been observed for layered niobates ($K_4Nb_6O_{17}$) intercalated with transition metals[3]. It has been also shown that a small amount of Cr_2O_3 on the TiO_2 surface acts a catalyst for hydrogen evolution upon illumination with UV light[4]. During UV-illumination semiconductor powders absorb photons, and electron-hole pairs are created inside the semiconductor, following which they can form sites for catalytic reaction. Similar behaviour can be expected from graphite intercalation compounds (GICs) which belong to the electron donor-acceptor system.

In the present work a novel photocatalyst originated from CrO_3-graphite intercalation compound (CrO_3-GIC) was examined in the reaction of water decomposition. The photocatalytic measurements were performed in dynamic conditions.

EXPERIMENTAL

Stage-3 CrO_3-GIC (I_c = 1.46 nm, C/Cr = 13.1) was prepared according to the procedure described previously[5-7]. Natural graphite from Kropfmühl AG, Germany (99.98 wt.% C flakes < 63 µm), was used as a host matrix. A mixture of 10 g graphite and 30 g CrO_3 in 100 cm^3 glacial acetic acid was refluxed for 2 hrs. The product of intercalation was washed with cold acetic acid and acetone and then dried to a constant weight. CrO_3-GIC was then subjected to reduction in K-naphtalenide/anhydrous THF solution (the concentration of K $\cong$ 0.5 M). The product of reduction (CrO_3-GIC/K) was than washed with water-ethanol solution to remove unreacted K and dried to a constant weight. The photocatalytic activity of CrO_3-GIC/K in the reaction of water decomposition was examined in an apparatus depicted in Fig. 1. The X-ray diffraction (XRD) measurements were performed to determine the structural changes effected in the CrO_3-GIC precursor due to its reduction (Fig. 2) whereas the concentration profiles for intercalates in both CrO_3-GIC and CrO_3-GIC/K were observed using the scanning electron microscopy (SEM) coupled with energy dispersive X-ray EDX) analyser (Fig. 3). All photocatalytic measurements were carried out at 20 °C. The flow reactor was irradiated using a mer-

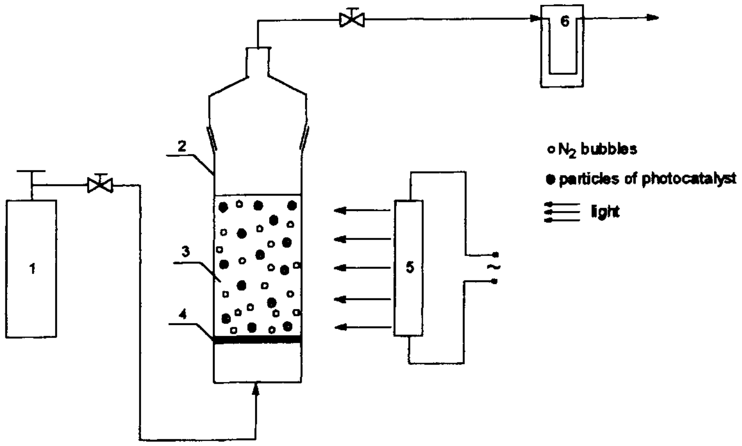

FIGURE 1 Schematic view of apparatus for the photocatalytic production of hydrogen on the CrO_3-GIC/K photocatalyst in the reaction of water decomposition. (1) nitrogen cylinder; (2) quartz reactor; (3) 100 cm^3 of deionized water with photocatalyst particles; (4) gas permeable membrane; (5) mercury UV-lamp; (6) flowmeter.

cury lamp of 180 W with the following light distribution: UV-A (< 302 nm) - 140 W/m^2, UV-B (302-366 nm) - 71.5 W/m^2 and UV-C (> 366 nm) - 12.1 W/m^2. Photocatalyst (0.04 g) was dispersed in pure deionized water by flowing a high purity nitrogen (0.6 dm^3/h). More details related to the activity tests are given in Fig. 1. The amount of hydrogen evolved was monitored by a gas chromatography.

RESULTS AND DISCUSSION

As seen from the XRD pattern given in Fig. 2a, the CrO_3-GIC precursor is stage-3 compound admixed with a small amount of stage-4 structure and the phase of pristine graphite. The following structural parameters of the dominant stage-3 CrO_3-GIC were ascertained from the family of peaks given in Fig. 2a: I_c = 1.4508 nm, d_i = 0.7808 nm and the thickness of intercalate layer Δd = 0.4458 nm. On considering Fig. 2b, it is clear that most of diffraction peaks arising from the CrO_3-GIC precursor disappeared on the XRD pattern of the product of reduction. Only residual peaks (d = 0.360 nm, d = 0.2965

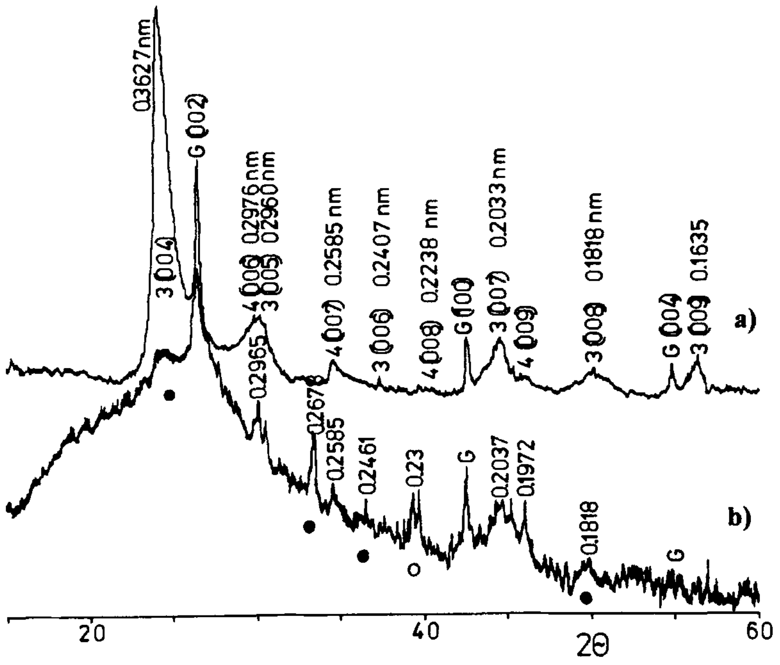

FIGURE 2 XRD patterns recorded for (a) the CrO_3-GIC precursor and (b) the CrO_3-GIC/K photocatalyst. CuKα radiation. ●, Cr_2O_3; o K_2O.

nm, d = 0.2037 nm, d = 0.1818 nm) associated with stage-(3+4) CrO_3-GIC are observed. The graphite peaks, (002) with d = 0.334 nm and (100) with 0.2128 nm, become very broad and weak. From comparison of the XRD patterns depicted in Figs. 2a and 2b, it is evident that the graphite structure comes to a high degree of destruction during the reducing reaction whereas the original CrO_3-GIC persisting in the graphite matrix does not undergo the stage transformation. The other peaks present in Fig. 2b may be ascribed to the products of reduction, such as Cr_2O_3 and K_2O, retained at the grain boundaries and/or encapsulated within the warped graphene layers. This presumption is supported by the EDX analysis (Fig. 3). A good coincidence of the distribution lines for Cr and K observed for the CrO_3-GIC/K photocatalyst proves that potassium solvated with THF readily invades the interlayer spacings of graphite filled with CrO_3 following the redox reaction. As a result of the re-

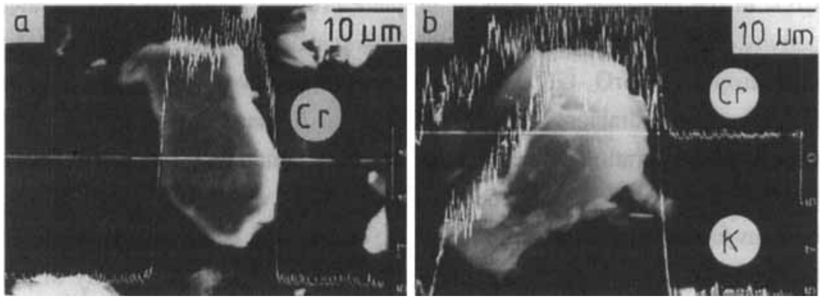

FIGURE 3 SEM micrographs with superimposed EDX distribution lines for (a) the CrO_3-GIC precursor and (b) the CrO_3-GIC/K photocatalyst.

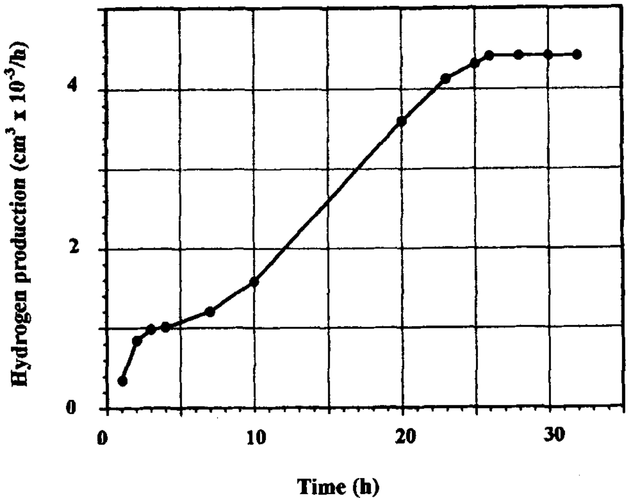

FIGURE 4 Hydrogen production on the CrO_3-GIC/K photocatalyst during the reaction of water decomposition. Nitrogen flow, 0.6 dm^3/h; weight of CrO_3-GIC/K photocatalyst, 0.04 g.

action occurring in the graphite gallery, the ultrafine particles of Cr_2O_3 and K_2O existing between the distorted and disrupted graphite layers may act as a complex catalyst.

The changes in the physics and chemistry of GIC due to reduction of

CrO_3 in the interlayer spacings of graphite brought about the photocatalytic activity of the material in the reaction of water decomposition. The evolution of hydrogen on CrO_3-GIC-based catalyst was observed during UV-illumination of water at ambient temperature (Fig. 4). A characteristic feature of the process is acceleration of the reaction rate with illumination time. After twenty five hours the hydrogen volume attains a constant value and catalytic activity remains further unchanged (4.4×10^{-3} cm^3/h). Such a behaviour of the examined material might suggest that during the reaction either the activity of photosensitive sites increases due to autocatalytic effect or inactive sites caged in the graphite pockets are disclosed due to hydrogen evolution. The experimental data do not allow us to indicate unequivocally which of the mentioned factors plays more important role, thus further studies on the long-time changes in the structure and composition of CrO_3-GIC/K photocatalyst should be continued.

In summary, it is worth noting that in contrast to the original CrO_3-GIC readily deintercalated in aqueous media[8], CrO_3-GIC/K exhibits a high chemical stability in water which is prognostic of its practical application as photocatalyst.

Acknowledgements

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References

[1.] A. Kudo et al., *J. Catal.*, **120**, 337 (1989).
[2.] K. Domen, J. Yoshimura, T. Sekine, A. Tanaka and T. Onishi, *Catal. Lett.*, **4**, 339 (1990).
[3.] K. Domen, A. Kundo, A. Tanaka and T. Onishi, *Catalysis Today*, **8**, 77 (1990).
[4.] A. Sobczyński, *J. Mol. Catal.*, **39**, 43 (1987).
[5.] N. Platzer and B. de la Martinière, *Bull. Soc. Chim. Fr.*, 197 (1961).
[6.] J. M. Skowroński, *Synth. Met.*, **73**, 21 (1995).
[7.] J. M. Skowroński, *J. Phys. Chem. Solids*, **57**, 695 (1996).
[8.] J. M. Skowroński, in *Handbook of Organic Conductive Molecules and Polymers*, edited by H. S. Nalwa, (John Wiley and Sons, Ltd, Chichester, 1997), Vol. 1, Chap. 12, pp. 621-686.