Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 175 (2005) 89–93

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Hydrogen evolution by photocatalysis of methanol vapor over Ti-beta

Wenquan Cui[a,b,*], Chenghua Xu[a], Shudong Zhang[a,b], Liangrong Feng[a], Shaojie Lü[a], Fali Qiu[a]

[a] *Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, PR China*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing, PR China*

Received 29 October 2004; received in revised form 23 February 2005; accepted 20 April 2005
Available online 24 May 2005

Abstract

In the present work, Ti-beta was prepared through the gas–solid reaction of beta with vapor $TiCl_4$, and characterized by means of XRD, FT-IR and UV–vis diffuse reflectance. Titanium atoms have been incorporated into the framework of beta, and no TiO_2 species was detected in Ti-beta. The photocatalytic activity of hydrogen evolution by UV-photocatalytic decomposition of methanol gas over Ti-beta was examined in a continues-flow quartz reactor at room temperature. The amount of hydrogen evolution per Ti-ion surface on Ti-beta is much higher than that of TiO_2 and TiO_2/beta. The titanium atoms incorporate into the framework of beta are the photocatalytic active centers.

Keywords: Ti-beta; Hydrogen evolution; Photocatalytic; Methanol; Gas–solid reaction

1. Introduction

Hydrogen is one of the most important clean fuels applied in non-polluting vehicles, domestic heating, and aircraft. Therefore, the studies on the hydrogen evolution via photocatalytic decomposition of water have been attracted much attentions in the recent years. As we know, semiconductor materials such as TiO_2 [1], $SrTiO_3$ [2–4], $K_4Nb_6O_{17}$ [5], $Na_2Ti_6O_{13}$ [6], $BaTi_4O_9$ [7], ZrO_2 [8], Ta_2O_5 [9] and $K_2La_2Ti_3O_{10}$ [10] have been widely applied in the photocatalysis fields. At the same time, most of them need to be loaded the other co-catalysts in order to enhance their activity. Even so, these semiconductor photocatalysts still exhibits very low photocatalytic activities due to their low efficiency in the formation of photoexcited charge that transfers to the surfaces [11].

On the other hand, there have been several studies regarding photocatalysts enclosed in the cage of zeolites. The enclosed photocatalysts vary from metal complexes to fine particles of semiconductors [12–15]. And photocatalysts have been also expected to disperse in isolation in the framework of zeolites. For examples, a kind of new zeolite material TS-1 was applied in CO_2 photocatalytic reduction to CH_4 with H_2 [16], and ZSM-5 was used as the photocatalyst for the decomposition of organic compounds [17]. Zeolite beta possesses a three-dimensional system of large 12-membered ring channel [18]. This gives beta interesting potential applications in acid-catalysed reactions where high thermal and hydrothermal stability and low steric restrictions can be of paramount importance. Another interesting potential application for beta is immobilization of chiral complex over it. Ti-beta zeolite was obtained by Ti incorporate into the framework of beta zeolite. Owing to its isolated framework Ti atoms and unique large-pore channel system, Ti-beta is an active catalyst for the selective oxidation of organic compounds with either organic hydroperoxides [19] or hydrogen peroxide [20] as oxidants. According to the photocatalytic properties of TS-1, Ti-beta will probably be a potential material as photocatalyst. However, there have been no reports on the application in the photocatalysis of Ti-beta, especially as a photocatalyst in hydrogen generation.

Methanol is a perfect hydrogen resource, and its successful application in photocatalytic decomposition to evolve hydro-

---

[*] Corresponding author. Tel.: +86 28 85250389; fax: +86 28 85223978.
E-mail addresses: ciocwq@hotmail.com, wkcui@163.com (W. Cui).

1010-6030/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2005.04.020

gen will be an ideal process. However, the recent researches have been mostly focused on the liquid water-methanol system [21–24]; few reports have been given about the photocatalytic decomposition of methanol gas [25].

In view of these, the present work reported synthesis of Ti-beta using the gas–solid reaction of beta with gas $TiCl_4$, investigated its photocatalytic property in the decomposition of methanol gas to hydrogen in a continuous-flow reactor, and also compared its activity per Ti-ion surface with the other photocatalytic materials, such as TiO_2, TiO_2/beta and so on.

2. Experimental procedures

2.1. Ti-beta preparation

Ti-beta was synthesized by the gas–solid reaction of beta (supplied by Nankai Share Group, China) with $TiCl_4$. The typical procedure was as follows: beta was loaded into a quartz reactor and heated to 500 °C for 4 h in a flow of dry nitrogen. The dehydrated samples were then kept at 600 °C and exposed to a flow of dry nitrogen bubbled through the vessel containing $TiCl_4$. After the $TiCl_4$ flow was continued for a desired time, the dry nitrogen flow was demanded to remove the residual $TiCl_4$. Afterwards, the obtained titanium-containing beta samples were treated at 600 °C by the wet nitrogen stream.

For comparison, the catalysts represented with TiO_2/beta were prepared by mechanical mixing of the parent beta with TiO_2 (Panzhihua Group, anatase, 46 nm) powder, which contained the same Ti content as the above-prepared Ti-beta.

2.2. Characterizations

The Ti and Al content of the samples were obtained by hydrogen peroxide color comparimetry on a 751G spectrometer and EDTA titration, respectively. The X-ray power diffraction chart was performed using a D/max-γ X-ray diffractometer with a Cu Kα source. FT-IR spectra were recorded on a 200SXV FT-IR spectrometer; 1 wt% samples were ground with potassium bromide powder and pressed into wafers. UV–vis diffuse reflectance spectra were obtained on a Hitachi UV-340.

2.3. Photocatalytic reaction

Photocatalytic reaction, irradiated by a low-pressure mercury lamp (4 W, main wavelength: 254 nm), was carried out in an interlayer quartz-reactor 6 ml capacity as shown in Fig. 1. Photocatalysts were loaded into interlayer of the reactor. The loaded amount of the photocatalysts in the reactor was as follows: TiO_2 3 g, TiO_2/beta 1.6 g, beta 1.6 g and Ti-beta 1.6 g. The whole system was a continuous-flow system; gaseous methanol was introduced into the quartz-reactor by Ar after the complete displacement of air in the system by Ar. The products H_2 and CO were analyzed by an on-line gas chromatography (TCD, TDX-01 Carbon Molecule Sieves Column, Ar carrier).

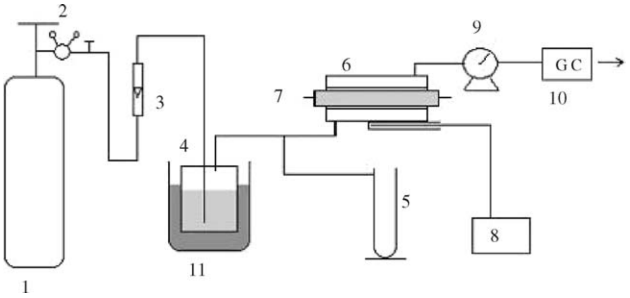

Fig. 1. Reaction flow chart: (1) Ar; (2) reduction valve; (3) flowrator; (4) bubbler; (5) pressure gauge; (6) quartz reactor; (7) low pressure mercury lamp; (8) temperature apparatus; (9) wet flowrator; (10) gas chromatogram; (11) water bath.

3. Results and discussion

3.1. Elements analysis

The results about Al and Ti contents of beta and Ti-beta is shown in Table 1. It can be clearly seen beta has no change on the ratio of SiO_2/Al_2O_3 during preparation of Ti-beta through the reaction with $TiCl_4$ gas. It indicates that titanium incorporation into the framework is mainly carried out through the $TiCl_4$ reaction with Si–OH groups existed in the molecular sieves, not the replacement of framework Al [26]. The results in Table 1 illustrate that the incorporated amount of Ti is presented by the ratio of SiO_2/TiO_2 being 50.

3.2. FT-IR and UV–vis spectra

Fig. 2 shows the FT-IR spectra of the beta and Ti-beta which was prepared by the reaction of beta with $TiCl_4$ gas. Meanwhile, we can see that Ti-beta has very similar FT-IR spectra to beta, which shows that Ti-beta still keeps its basic framework during the reaction. For beta, there is a weak absorption at 960 cm^{-1} which is due to silanol groups of defective sites [27,28]. However, the intensity of the absorption peak at 960 cm^{-1} for Ti-beta is increased. It is attributed to the flex vibration of Si–O bond which connects to the $(O_3SiO)_3Ti$– or Ti=O [24]. This strong peak is considered to be characteristic of titanium-containing molecular sieves in literature [18] in TS-1. The increase in intensity of the ab-

Table 1
The chemical composition of samples

Sample	SiO_2/Al_2O_3	SiO_2/TiO_2
Beta	69	–
Ti-beta	69	50
TiO_2/beta	69	50