

Hydrogen evolution by photocatalysis of methanol vapor over Ti-beta

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Abstract

In the present work, Ti-beta was prepared through the gas–solid reaction of beta with vapor TiCl₄, 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 TiO₂ 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 continuous-flow quartz reactor at room temperature. The amount of hydrogen evolution per Ti-ion surface on Ti-beta is much higher than that of TiO₂ and TiO₂/beta. The titanium atoms incorporate into the framework of beta are the photocatalytic active centers.

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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 TiO₂ [1], SrTiO₃ [2–4], K₄Nb₆O₁₇ [5], Na₂Ti₆O₁₃ [6], BaTi₄O₉ [7], ZrO₂ [8], Ta₂O₅ [9] and K₂La₂Ti₃O₁₀ [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 CO₂ photocatalytic reduction to CH₄ with H₂ [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-

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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 (Panzhuhua 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 $K\alpha$ 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

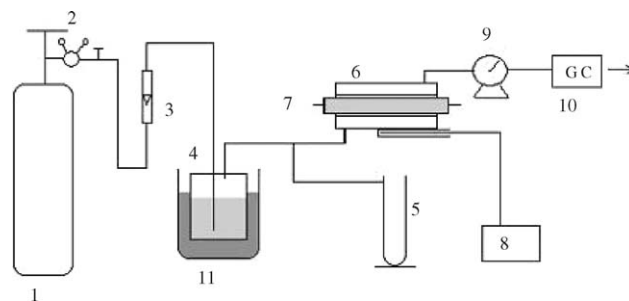


Fig. 1. Reaction flow chart: (1) Ar; (2) reduction valve; (3) flowrator; (4) bubbler; (5) pressure gauge; (6) quartz reactor; (7) low pressure mercury lamp; (8) temperature apparatus; (9) wet flowrator; (10) gas chromatogram; (11) water bath.

products H_2 and CO were analyzed by an on-line gas chromatography (TCD, TDX-01 Carbon Molecule Sieves Column, Ar carrier).

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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 $\text{SiO}_2/\text{TiO}_2$ 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 $(\text{O}_3\text{SiO})_3\text{Ti}$ – or $\text{Ti}=\text{O}$ [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	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{SiO}_2/\text{TiO}_2$
Beta	69	–
Ti-beta	69	50
TiO_2/beta	69	50

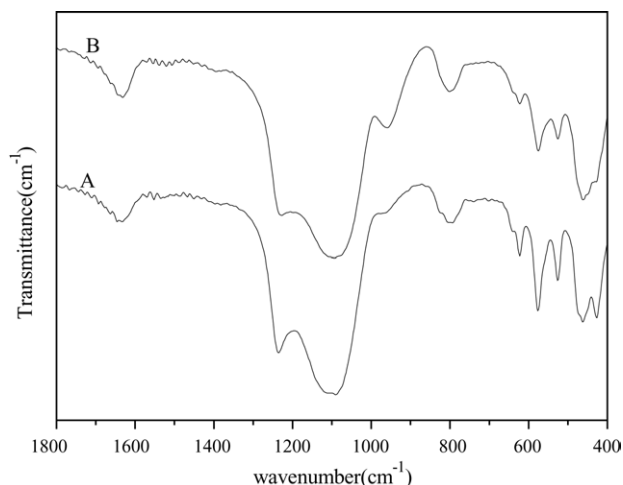


Fig. 2. FT-IR spectra of (A) beta and (B) Ti-beta.

sorption at 960 cm^{-1} in Ti-beta also indicated that titanium atoms are able to incorporate into the framework of beta to form the framework titanium [27,28].

The UV–vis diffuse reflectance spectra of Ti-beta, beta, TiO_2/beta and of a pure TiO_2 (anatase) powder are shown in Fig. 3. From it, only a sharp band at ca. 225 nm can be clearly observed in the spectrum of Ti-beta, this band has been assigned to the ligand-to-metal charge transfer (CT) of the isolated titanium atoms. The sample beta shows no absorption in 200–300 nm. The spectrum of TiO_2/beta exhibits an evident shoulder in the 220–350 nm range. Its trend is close to the spectrum of anatase TiO_2 . So this shoulder can be assigned to dispersed Ti-oxo species. Therefore, the situation of titanium atoms in TiO_2/beta is expected to be in the formation of TiO_2 crystalline, but for Ti-beta the titanium atoms exist in the formation of the isolated framework Ti.

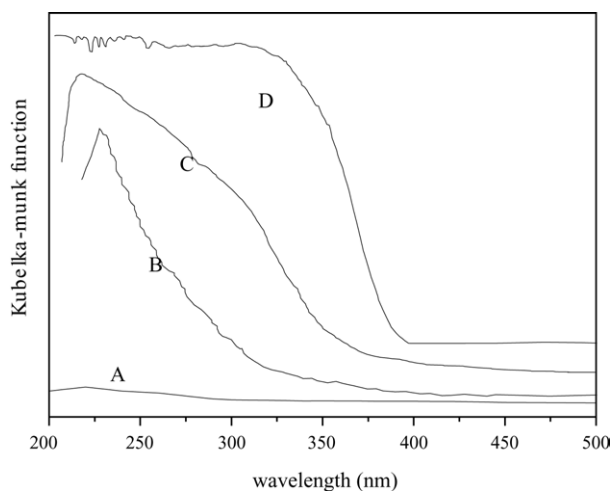


Fig. 3. UV–vis diffuse reflectance spectra of (A) beta zeolite, (B) Ti-beta, (C) TiO_2/beta and (D) TiO_2 .

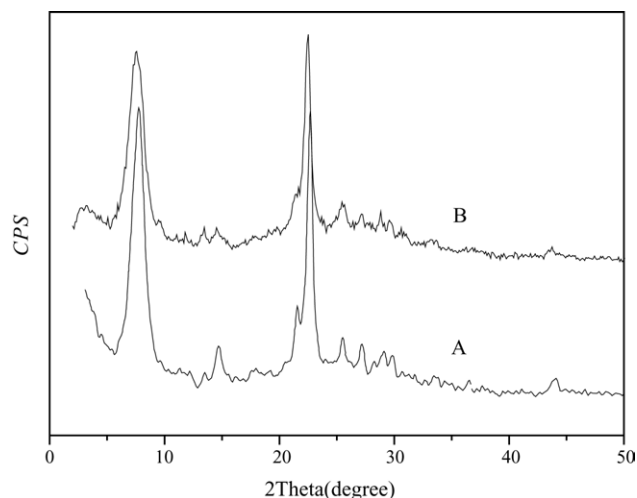


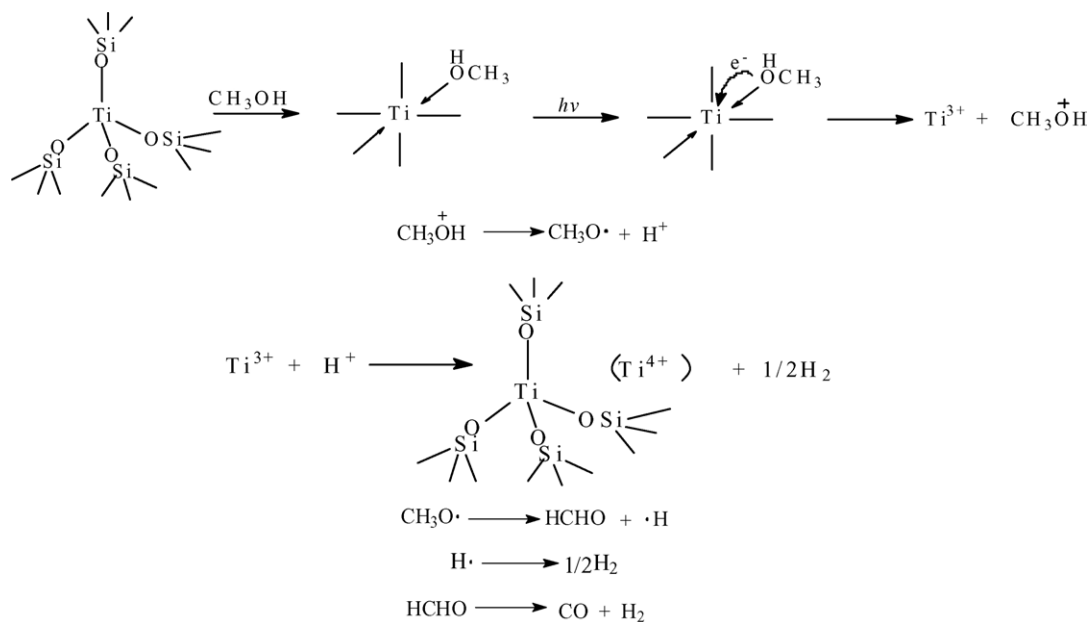
Fig. 4. XRD spectra of (A) beta and (B) Ti-beta.

3.3. XRD spectra

Fig. 4 shows the XRD spectra of beta and Ti-beta. It can be easily seen that Ti-beta exhibits the same spectra as beta. A strong peak at around $2\theta = 22^\circ$, indicative of BEA structure, is observed in both samples. This further indicates that the structure of beta is not changed during the reaction with TiCl_4 vapor. The main peaks of diffraction pattern B at around $2\theta = 8^\circ$ and 22° shift toward lower diffraction angle, compared to those of the pattern A. In tetrahedral configuration, the Ti–O bond length, $d_{\text{Ti-O}}$, is longer than the Si–O bond, $d_{\text{Si-O}}$ (1.76 and 1.59 Å, respectively), causing the lattice to expand slightly upon incorporation of Ti. So, the incorporation of titanium can be monitored by the change in the unit cell volume [29]. Therefore this result can be taken as an evidence of Ti incorporation into the zeolite framework [20]. At the same time, the absence of peak at $2\theta = 25.4^\circ$ further makes out that no detectable titanium dioxide is found in the Ti-beta. According to XRD and UV–vis diffuse reflectance of Ti-beta, titanium atoms have been proved to incorporate into the framework of molecular sieves after the reaction with TiCl_4 vapor and be free from anatase TiO_2 .

3.4. Photocatalytic properties

In the present work, the photocatalytic activity of Ti-beta is evaluated by photocatalytic decomposition of methanol gas to hydrogen in a continuous-flow quartz-reactor. At the same, its activity has been also compared with TiO_2/beta , TiO_2 and beta, respectively. The amount of hydrogen evolution on Ti-beta was 0.01204 mmol/g after illuminating 3 h, and it was as about 10 times as that on beta whose photocatalytic activity was 0.00127 mmol/g. In order to exhibit the characteristic properties of active sites in Ti-beta, we compare the photocatalytic activity of per surface a Ti-ion among Ti-beta, TiO_2/beta and TiO_2 as shown in Fig. 5. From Fig. 5, it can be clearly observed that all catalysts give an activity for the pho-



Scheme 1.

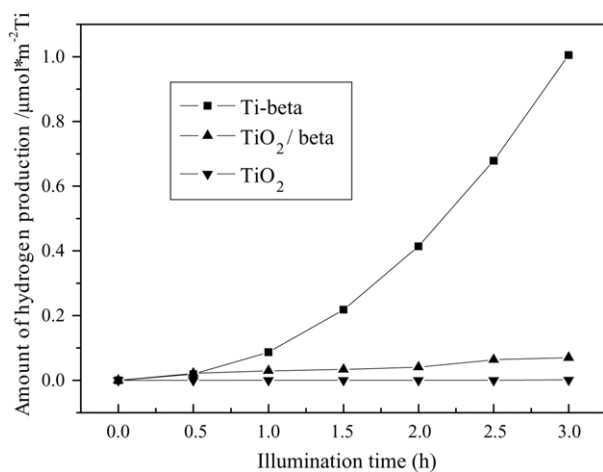


Fig. 5. Amount of hydrogen production of per surface a Ti-ion among Ti-beta, TiO₂/beta and TiO₂. (29% methanol in Ar; light source: 4W low-pressure mercury lamp; reaction cell: inner irradiation quartz cell.)

photocatalytic decomposition of methanol to hydrogen. Among them, Ti-beta shows much higher photocatalytic activity per Ti-ion surface than that of TiO₂/beta and TiO₂.

3.5. Discussions

From these results above, it is clearly demonstrated that the titanium atoms in Ti-beta framework structure can absorb the photons and photocatalytically decompose the absorbed methanol gas on the Ti-beta.

In the photocatalytic reaction using TiO₂, electron and hole in conduction and valence bands formed via photo-excitation of TiO₂ contribute to the reduction and oxidation reactions, respectively. However, the positive hole and electron are easily recombined in a very short time, which will there-

fore lead to a very low activity of the photocatalyst. On the other hand, in a photocatalytic reaction using Ti-beta, charge transfer excitation in the Ti atoms, $\text{Ti}^{4+}-\text{O}^{2-} \rightarrow \text{Ti}^{3+}-\text{O}^-$, is expected to lead to photocatalytic reactions [30].

The high photocatalytic activity of the Ti-beta catalyst also may be attributed to absorption of large amount of methanol to Ti-beta in which Ti atoms are highly dispersed in beta as well as the microporous structure which enables all Ti atoms in Ti-beta to act as reaction active sites. When methanol is datively bonded to intra-framework Ti in Ti-beta to give six-fold coordinated Ti species, charge transfer (CT) transition in the dative bond of Ti–O may lead to the oxidation of CH₃OH and the formation of H₂. In our work, the products including H₂ and CO were detected by GC. According to the detected products, the possible mechanisms of photocatalytic decomposition of methanol gas were deduced as shown in Scheme 1.

4. Conclusions

This present work uses the gas–solid reaction of beta with vapor TiCl₄ to obtain Ti-beta photocatalyst for decomposition of methanol gas. From the results of test, the following conclusions can be drawn:

- (1) Ti-beta is prepared by treating beta with the vapor of TiCl₄. The characterizations by means of XRD, FI-IR and UV–vis diffuse reflectance show that titanium atoms are contained in the framework of beta zeolites.
- (2) The amount of hydrogen evolution per Ti-ion surface on Ti-beta is much higher than that of TiO₂ and TiO₂/beta. The titanium atoms incorporate into

the framework of beta are the photocatalytic active centers.

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