Photocatalytic generation of hydrogen on Zr-MCM-41

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Abstract

Zr-MCM-41 was prepared via incorporation of Zr into the amorphous wall of MCM-41 in the hydrothermal synthesis process. Experimentally, photocatalytic generation of hydrogen on Zr-MCM-41 was investigated in a total reactivity system. In the presence of Zr-MCM-41, hydrogen yield (22.4 μmol H2/h) in the photocatalytic decomposition of H2O was highly enhanced by at least 2.5 times over that of the conventional photocatalyst ZrO2. The enhancement may be due to the high dispersion of ZrO2 and the justified band gap between the conduction band and valance band of ZrO2 in the wall of MCM-41. This work demonstrates how photodecomposition of H2O was affected by high dispersion of photoactive species (ZrO2) in the amorphous wall of MCM-41. © 2002 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Photocatalysis; Zr-MCM-41; Clean energy

1. Introduction

Hydrogen is one of the most important chemicals in the industrial commodity. Hydrogen is mainly consumed in the hydrotreating and synthesis of ammonia, methanol, higher alcohols and aldehydes processes. Generation of hydrogen via photocatalytic decomposition of water has attracted much attention from the viewpoint of conversion of solar energy into chemical fuels.

Recently, photocatalytic formation of hydrogen and oxygen on semiconductors such as TiO2 [1,2], SrTiO3 [3] and ZrO2 [4] has been widely investigated. Photocatalytic decomposition of H2O on TiO2 catalysts is not very effective simply because its reduction potential of electrons in the TiO2 conduction band is almost the same as that of H2/H2O (E = 0 eV NHE, pH = 0) [4]. The photocatalysis behavior of ZrO2 with a highly negative flat-band potential (Efb = −1.0 eV NHE, pH = 0) and the wide band gap (Ebg = 5.0 eV) is very different from that of TiO2. However, these semiconductor photocatalysts possess a very low efficiency in the formation of photoexcited charge that transfers to the surfaces to initiate the decomposition of H2O.

In 1992, Mobil’s scientists [5] successfully synthesized a new family of mesoporous silicate and aluminosilicate molecular sieves, designated as M41S. M41S including MCM-41 (hexagonal), MCM-48 (cubic) and MCM-50 (laminar) synthesized with liquid crystal templates possesses a well-order array of structure and a uniform pore size distribution engineered in the range from 15 to 100 Å. In addition, M41S has physical properties of high thermal and hydrothermal stability, large surface area (over 700 m2/g), and hydrocarbon sorption capacities of 0.7 ml/g and greater. M41S is generally considered as excellent catalysts, or catalyst supports. MCM-41, possessing a hexagonal arrangement of channels, is the most important member of the M41S family. The wide and uniform unidimensional channels of MCM-41 allow a faster diffusion of larger organic molecules than the microporous zeolite and aluminophosphate-based materials with channels and cavities only up to 15 Å in diameters. Furthermore, the pore size of MCM-41 can be systematically varied in the range of 15–100 Å by simply adjusting the synthesis conditions. MCM-41 is highly thermal stable with a very high surface area of > 900 m2/g [6].

It is well known that incorporation of photoactive elements into molecular sieves may exhibit a high photocatalytic activity because of the high dispersion state of the photoactive species in the zeolite framework and the
prolonged separation of electrons and holes [7,8]. Zhang [9] also indicated that Ti-substituted zeolites could initiate decomposition of NO under UV irradiation. In addition, Ti-substituted zeolites have a high reactivity and selectivity for production of CH3OH in photocatalytic reduction of CO2 with H2O [7].

MCM-41 possesses a hexagonal crystalline structure with an adjustable mesopore size of 15–100 Å. Photoactive species (such as Zr and Ti) can be easily incorporated into the amorphous wall. In a preliminary study, we found that a high dispersion of Ti–O moieties in the framework of MCM-41 could enhance the photocatalytic decomposition of H2O if compared with the bulk TiO2. ZrO2 is a promising light harvesting agent because its conduction band locates at a much higher energy level than most other semiconductors [10]. Thus, the main objective of the present work was to study the enhancement of photocatalytic generation of hydrogen effected by Zr-MCM-41.

2. Experimental

Fumed silica (Sigma) and sodium silicate solution (14% NaOH and 27% SiO2) were used as silica sources in the synthesis of MCM-41. Hexadecyltrimethylammonium bromide (CTABr) and tetramethylammonium hydroxide (TMAOH) (25%, Lancaster) were used as a template and a mineralizer, respectively. 9.6 g of the TMAOH solution and 23.4 g of CTABr were well mixed in 100 g of water with stirring until the solution was clear. 5.67 g of sodium silicate and 45.2 g silica were then added and stirred for about 2 h. The pH value of the solution was adjusted in the range of 10.5–11.0 with a 0.4N diluted sulfuric acid and stirred for additional 30 min. The molar composition of main species in the solution was 0.33 (CTABr):0.95 (TMAOH):41.9 (H2O):10.0 (SiO2). About 1–5% of zirconium isopropoxide was added in the MCM-41 mother solution for preparation of the Zr-MCM-41 catalyst. The mixture gel was heated in a Teflon-lined stainless-steel autoclave at 423 K for 48 h. The as-synthesis solid materials were dried in air at 373 K for 16 h and calcined at 823 K for 8 h to decompose the templating materials.

Structure of catalysts was determined by X-ray powder diffraction (XRD, RIGAKU Model D/MAX III-V) spectroscopy with CuKα radiation. N2 adsorption–desorption isotherms of catalysts were conducted at 77 K in the Micromeritics instrument (ASAP 2010). Samples were degassed at 673 K for 12 h prior to measurements. Pore size and surface area of the catalysts were determined by the Barrett–Joyner–Halenda (BJH) [11] and the Brunauer–Emmett–Teller (BET) methods, respectively. The dispersion of Zr in MCM-41 was studied by diffuse reflectance UV–VIS (DR UV–VIS) spectroscopy. The DR UV–VIS is very sensitive for the presence of extraframework and coordination of metals in MCM-41.

The synthesized MCM-41 with a relatively well-defined X-ray diffraction pattern is shown in Fig. 2. The (1 0 0) peak with repetition distance of pores (d100) can be indexed on a hexagonal lattice with a pore diameter of about 45 Å. As expected, the XRD characteristic peaks for ZrO2 were not observed in the Zr-MCM-41. The structural parameters of the synthesized MCM-41 (d100 spacings and the unit cell parameter (a0)) are listed in Table 1. X-ray diffraction patterns of the Zr-MCM-41 catalysts with a Si/Zr atomic ratio of 80 are also shown in Fig. 2. It is clear that the Zr-MCM-41 catalyst containing four low-angle features ((1 0 0), (1 1 0), (2 0 0), (2 1 0)) in the XRD patterns possessed a MCM-41 hexagonal characteristic pore structure. Furthermore, incorporation of a small amount of zirconia into MCM-41 would cause little distortion of the framework of the mesoporous zeolite. However, the (1 0 0) peak of the Zr-MCM-41 with the higher zirconia content shifted towards small 2θ angles that suggested a reduced regularity of silicate framework of the MCM-41.

The N2 adsorption–desorption isotherms of the MCM-41 and Zr-MCM-41 catalysts show an inflection characteristic
Fig. 2. Powder X-ray diffraction patterns of (a) Zr-MCM-41 (Si/Zr = 80) and (b) MCM-41.

Table 1
Properties of the photocatalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Zr</th>
<th>(d_{100}) (Å)</th>
<th>(a_0) (Å)</th>
<th>(d_p) (Å)</th>
<th>SA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-MCM-41</td>
<td>80</td>
<td>45.7</td>
<td>52.8</td>
<td>37.9</td>
<td>562</td>
</tr>
<tr>
<td>MCM-41</td>
<td></td>
<td>41.1</td>
<td>32.0</td>
<td>841</td>
<td></td>
</tr>
<tr>
<td>ZrO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18</td>
</tr>
</tbody>
</table>

*a*Unit cell parameter: \(a_0 = 2d_{100}/3^{1/2}\).

*b*dₚ: Average pore diameter.

*c*SA: BET surface area.

of capillary condensation within the mesopores (see Fig. 3). For the mesoporous zeolite MCM-41, the inflection occurred at \(P/P_0\) of 0.2–0.4. By using the BJH model calculation, the pore diameter of the Zr-MCM-41 was 37.9 Å (Table 1). The BET surface area of the Zr-MCM-41 catalyst was about 562 m²/g.

Dispersion of zirconium in MCM-41 was measured by diffuse reflectance UV-visible (DR UV–VIS) spectroscopy. The DR UV–VIS spectra of the Zr-MCM-41, MCM-41 and ZrO₂ are shown in Fig. 4. The band gap of Zr-MCM-41 was increased to 5.0 eV due to the blue-shift for the absorption of Zr-MCM-41 compared to that of ZrO₂. In addition, the absorption intensity of the Zr-MCM-41 catalyst was, as expected, much intense than that of the MCM-41. A single narrow band at 205 nm was observed indicating that zirconium might be highly dispersed in MCM-41. It is very likely that most of the zirconium atoms were incorporated into the amorphous wall of the MCM-41 hexagonal structure. Little UV/VIS absorption was observed for MCM-41 at 200–400 nm.
Hydrogen yields for photocatalytic decomposition of water catalyzed by Zr-MCM-41 and ZrO$_2$ are shown in Fig. 5. The hydrogen yields increased as the photocatalytic time increased (under 400 W UV irradiation). Photodecomposition of H$_2$O may not be initiated without a catalyst or UV irradiation. On Zr-MCM-41 catalyst, accumulated 112 μmol of hydrogen were yielded in a 5 h photocatalytic reaction. It is clear that the photodecomposition of H$_2$O was enhanced by the zirconium in the framework of MCM-41. Interestingly, the enhancement was about 2.5 times over that on the ZrO$_2$ photocatalyst. The enhancements of H$_2$O decomposition for the hydrogen yield may be due to at least two possibilities: (1) the high dispersion of ZrO$_2$ in the amorphous wall of MCM-41 and (2) the modified band gap between the conduction band and valance band of ZrO$_2$ in MCM-41. By the onset of the diffuse reflectance spectrum (250 nm), the band gap of Zr-MCM-41 was estimated to be 5.0 eV that was wider than that of ZrO$_2$. The valence bands of the photocatalyst may be formed by 2p orbitals of O$^{2-}$. These indicate that the conduction band of the Zr-MCM-41 is more negative than that of ZrO$_2$. The potential of the excited electrons for photodecomposition of H$_2$O is higher than that of ZrO$_2$. In addition, due to the wide band gap of Zr-MCM-41, the lifetime of photoluminescence of the Zr-MCM-41 was longer than that of bulk ZrO$_2$, that may lead to the enhancement of photodecomposition of H$_2$O.

4. Conclusion

Photodecomposition of H$_2$O on Zr-MCM-41 was enhanced by at least 2.5 times if compared with the conventional ZrO$_2$ photocatalyst in a total reflectance system. Highly dispersed ZrO$_2$ in the amorphous wall of MCM-41 (observed by DR UV–VIS spectroscopy) might justify the separation of the photoinduced electrons and holes. In addition, the lifetime of photoluminescence of the Zr-MCM-41 was greater than that of the bulk ZrO$_2$, that might also lead to the significant enhancement for photodecomposition of H$_2$O.

References