Photocatalytic decomposition of CCl₄ on Zr-MCM-41

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Abstract

Photocatalytic decomposition of CCl₄ (80 mg L⁻¹ in H₂O) effected by Zr-MCM-41 (Zr incorporated in the amorphous wall of MCM-41) has been studied in the present work. Experimentally, photocatalytic decomposition of CCl₄ on Zr-MCM-41 was enhanced by about 1.96 times over that on ZrO₂. Photocatalytic decomposition of CCl₄ may proceed via a two-electron transfer process that yields mainly CHCl₃, Cl⁻ and H₂. Since little C₂Cl₂, C₂Cl₆ or CH₂Cl₂ was found, it is unlikely that CHCl₃ involved in the secondary photocatalytic degradation process. In addition, photocatalytic splitting of H₂O on Zr-MCM-41 was also enhanced. The yield of H₂ was 6.5 mmol (g ZrO₂)⁻¹. About 68% of this hydrogen (6.5 mmol (g ZrO₂)⁻¹) was consumed in the photocatalytic decomposition of CCl₄.

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1. Introduction

CCl₄, a volatile organic compound (VOC), has been used as solvents in pharmaceutical, plastic, dye, oil, wax, cleaning, dry cleaning, paint and semiconductor industries [1]. CCl₄ with an estimated lifetime of roughly 40 years may cause depletion of stratospheric ozone [2]. It should be noted that CCl₄ might also cause adverse effects on the human health [1].

Photocatalytic decomposition of halogenated organic compounds in aqueous and gaseous phases is of increasing interest and importance [3,4]. Photoexcitation of TiO₂ can generate strongly oxidative VB (valence band) holes and moderately reductive CB (conduction band) electrons to initiate the photocatalytic decomposition of CCl₄ [5,6]. ZrO₂ appears to be a promising light harvesting agent since its CB locates at a much higher energy level than most other semiconductors [7,8].

In 1992, Mobil’s scientists [9] successfully synthesized a family of mesoporous silicate and aluminosilicate molecular sieves, designated as M41S. MCM-41 is one of the most important members of the M41S family. MCM-41 contains a hexagonal array of uniform mesopores but lack strict crystallographic order on the atomic level. 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 up only to 1.5 nm in diameters. Furthermore, the pore size of MCM-41 can be systematically varied in the range of 1.5–10 nm by simply adjusting the synthesis conditions. MCM-41 is highly thermal stable with a very high surface area of >900 m² g⁻¹ [10].

Generally, photocatalytic activities for molecular sieves incorporated with select transition metal elements may be enhanced because of the high dispersion of the photoactive sites in the framework of molecular sieves and an effective separation of electrons and holes [11]. In the separated experiments, we found that splitting of H₂O on photoactive elements (such as Zr or Ti) incorporated into the amorphous wall of MCM-41 was highly enhanced [12,13]. The enhancement was over 80 times if compared with the conventional photocatalyst ZrO₂. Since the
reduction potential of CCl₄ (−0.51 eV) [14] is less negative than the CB of ZrO₂, photocatalytic decomposition of CCl₄ on the dispersed ZrO₂ in MCM-41 is of great interest. Thus, the aim of the work reported here was to study the photocatalytic decomposition of CCl₄ in H₂O effected by Zr-MCM-41. The reaction path in the photocatalytic decomposition of CCl₄ and H₂O has also been investigated.

2. Experimental

In the synthesis of MCM-41, fumed silica and/or sodium silicate solution (Merck) (14% NaOH and 27% SiO₂) were used as Si sources. Hexadecyltrimethylammonium bromide ((CTA)Br, ACROS) and tetramethylammonium hydroxide (TMAOH, 25%, Lancaster) were used as a template and mineralizer, respectively. A solution (40 g L⁻¹) with a molar composition of 0.33 (CTA)Br:0.95 TMAOH:41.9 H₂O :1.0 SiO₂ was mixed with zirconium isopropoxide (Alfa) (Si/Zr = 80). The pH value of the solution was adjusted to 10.5–11.0 with a diluted sulphuric acid and stirred well with a magnetic stirring for 30 min. The mixture gel was heated at 423 K for 48 h in a Teflon-lined stainless-steel autoclave. The as-synthesis solid materials were filtered, washed with distilled H₂O, dried in air at 373 K for 16 h, and then calcined at 823 K for 8 h to decompose the templating materials. Chemical structures of the Zr-MCM-41 and ZrO₂ photocatalysts were characterized by X-ray diffraction (XRD) spectroscopy (Rigaku Model D/Max III-V) (scanned from 1.5° to 80° (2θ) with a scan rate of 4° min⁻¹). The absorption spectra of ZrO₂ and Zr-MCM-41 were also determined by diffuse reflectance UV–vis (DR UV–vis) spectroscopy. The powder samples were loaded in a quartz cell and their spectra were collected at 200–600 nm.

The photocatalytic decomposition of CCl₄ experiments were carried out in a quartz reactor (filled with 40 mL of H₂O) with a total reflection mirror system (shown in Fig. 1). Seven and 14 mg of Zr-MCM-41 and ZrO₂ (corresponding to 192 and 350 mg ZrO₂ in 1 L of H₂O), respectively were suspended in the CCl₄ (80 mg L⁻¹) aqueous solution (pH value 5.5) by magnetic stirring in the photocatalytic decomposition process. The reaction system was purged with nitrogen for 30 min prior to the UV–vis irradiation. The light source of a 500 W xenon arc lamp (ORIEL Instruments, Model 66028) with a water filter was used in the experiments. The distance from lamp to the reactor was about 15 cm. Photocatalytic decomposition of CCl₄ were conducted at 400 W for at least 5 h. The intensity of the incident light to the reactor was 25 mW/cm² measured by a power meter (Newport, model 818-LS-1).

Chlorinated compounds were analyzed using a purge-and-trap system (Tekmer LSC 2000) and a GC (Varian 3400) equipped with a ⁶³Ni electron capture detector and a SUPELCO column (1% SP TN 1000 support 60/80 CARBOP ACKTNB 243.8 cm × 0.3175 cm S.S.). Concentrations of Cl⁻ formed in the photocatalysis process were determined by ion chromatography (DIONEX 300). Gaseous samples were analyzed by a GC (Perkin-Elmer Auto System) equipped with a thermal conductivity detector and a Carboxen 1000 column.

3. Results and discussion

Chemical structures of the Zr-MCM-41 and ZrO₂ photocatalysts (studied by XRD) are shown in Fig. 2. The low angle and well-defined peaks at (1 0 0) and (1 1 0) was suggestive of a hexagonal mesopore system in the MCM-41. The (1 0 0) peak with a repetition distance of pores (d₁₀₀) can be indexed on a well-defined hexagonal lattice possessing a pore diameter of about 46.7 Å. The unit cell parameter (a₀ = 2d₁₀₀/√3) was about 53.9 Å. Since the wall of the MCM-41 was amorphous, incorporation of Zr into the wall framework of MCM-41 would be accessible. As expected, the XRD characteristic peaks for the bulk ZrO₂ phase were not observed in the Zr-MCM-41 sample. It seems that the incorporation of Zr into the amorphous wall of MCM-41 might be highly dispersed and caused little distortion of the hexagonal mesoporal structure of MCM-41.

The absorption spectra of the Zr-MCM-41 and ZrO₂ photocatalysts were also measured by DR UV–vis spectroscopy. In Table 1, a blue-shift of the absorption of Zr-MCM-41 from that of ZrO₂ is also observed. The band gap of Zr-MCM-41 is 4.92 eV. Since the overpotential of about 0.8 eV is required for an efficient CB electron transfer, it is also suggestive that Zr was incorporated and highly dispersed in the amorphous wall of MCM-41 [9,12].
Table 1
The maximum wavelength and band gap of Zr-MCM-41 and ZrO₂ determined by UV–vis spectroscopy

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Maximum wavelength (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-MCM-41</td>
<td>208</td>
<td>4.92</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>230</td>
<td>4.05</td>
</tr>
</tbody>
</table>

Note: The band gap (eV) was determined by the extrapolation of the rising portion of the absorption spectra to zero absorption (nm) [17].

The UV–vis irradiation time dependence for photocatalytic decomposition of CCl₄ (initial concentration = 80 mg L⁻¹) effected by ZrO₂ (350 mg ZrO₂ (kg H₂O)⁻¹) or Zr-MCM-41 (192 mg ZrO₂ (kg H₂O)⁻¹) is shown in Fig. 3. Without a photocatalyst, little CCl₄ was decomposed in the first 5 h. Accumulated 50% and 97% of CCl₄ was photocatalytically decomposed on ZrO₂ and Zr-MCM-41, respectively, under UV–vis irradiation for 5 h. Note that the Zr-MCM-41 possessed an enhanced photocatalytic decomposition of CCl₄ by at least 1.96 times if compared to the bulk ZrO₂. The enhancement for the photocatalytic decomposition of CCl₄ on Zr-MCM-41 may be due to at least two possibilities: (1) the high dispersion of ZrO₂ in MCM-41 may increase the number of photoactive sites and (2) the modified separation of CB electrons and VB holes of ZrO₂ moieties in MCM-41 prolongs the lifetime of photomiphosphorescence of ZrO₂ that might alter the reaction pathways and product selectivities and enhance the electron transfer in the photocatalysis process.

Generally, photocatalytic decomposition of CCl₄ may be initiated via two possible reaction paths: (1) formation of ·CCl₃ radicals and Cl⁻ and (2) through a two electrons process, forming CCl₃⁻ and Cl⁻ [14–17]. Interestingly, the yield of CHCl₃ was about 2.95 mmol (g ZrO₂)⁻¹ in the photocatalytic decomposition of CCl₄ on Zr-MCM-41 (Table 2). Table 2 also shows that the yield of H₂ in the photocatalytic decomposition of CCl₄ on Zr-MCM-41 was about 2.1 mmol (g ZrO₂)⁻¹. The CCl₃⁻ may react with H⁺ to form CHCl₃. Chio and Hoffmann reported that trace C₂Cl₆ was found in the photocatalytic decomposition of CCl₄ without electron donors [14]. In the present work, little C₂Cl₂, C₂Cl₆ or CH₂Cl₂ was observed, suggesting little CHCl₃ involved in the secondary photocatalytic degradation process. On the contrary, the yield of Cl⁻ on Zr-MCM-41 was about 2.2 times over that on ZrO₂ (Table 2). Cl⁻ may be formed via the CCl₄ reduction with the CB electrons generated from the photoexcitation of ZrO₂ and Zr-MCM-41.

We also found that photocatalytic splitting of H₂O to H₂ was enhanced on Zr-MCM-41 (Fig. 4). However, H₂ was also consumed in the photocatalytic decomposition of CCl₄ (Fig. 4). The yield of H₂ was about 6.5 mmol (g ZrO₂)⁻¹ in the photocatalytic splitting of H₂O on Zr-MCM-41 for 5 h. However, only 2.1 mmol H₂ (g ZrO₂)⁻¹ were yielded from the photocatalytic decomposition of CCl₄ on Zr-MCM-41. A possible mechanism for photocatalytic decomposition of CCl₄ effected by the suspended Zr-MCM-41 in H₂O is shown in Scheme 1. Photoexcitation of the Zr-MCM-41 generated oxidative VB holes and reductive CB electrons. The photocatalytic decomposition of CCl₄ may be initiated by two-electron process to form CCl₃⁻ and Cl⁻ on the photocatalyst surfaces. Thermodynamically, the two-electron transfer is known to be more favorable than that one-electron transfer process [14]. Simultaneously, H⁺ was formed via the photocatalytic decomposition of H₂O. Apparently, CCl₃⁻ reacted with H⁺ to form CHCl₃. Stoichiometrically, 68% of H₂ was consumed in

Table 2
The conversion and concentration (mmol (g ZrO₂)⁻¹) of by-products in the photocatalytic decomposition of CCl₄ (80 mg/L) on Zr-MCM-41 and ZrO₂ for 5 h irradiation

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Conversion</th>
<th>CHCl₃</th>
<th>Cl⁻</th>
<th>H₂</th>
<th>CH₂Cl₂</th>
<th>C₂Cl₂</th>
<th>C₂Cl₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-MCM-41</td>
<td>0.97</td>
<td>ND</td>
<td>1.73</td>
<td>2.13</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.50</td>
<td>ND</td>
<td>0.80</td>
<td>0.21</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND: not detectable.

Trace C₂Cl₆ was found in the photocatalytic decomposition of CCl₄ without electron donors [14]. In the present work, little C₂Cl₂, C₂Cl₆ or CH₂Cl₂ was observed, suggesting little CHCl₃ involved in the secondary photocatalytic degradation process. On the contrary, the yield of Cl⁻ on Zr-MCM-41 was about 2.2 times over that on ZrO₂ (Table 2). Cl⁻ may be formed via the CCl₄ reduction with the CB electrons generated from the photoexcitation of ZrO₂ and Zr-MCM-41.

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Fig. 3. Irradiation time dependence for the photocatalytic decomposition of CCl₄ (80 mg L⁻¹ in H₂O) effected by (a) Zr-MCM-41 (192 mg ZrO₂ (kg H₂O)⁻¹) and (b) ZrO₂ (350 mg ZrO₂ (kg H₂O)⁻¹) and (c) without a catalyst.

Fig. 4. The yield of H₂ (mmol (g ZrO₂)⁻¹) in the photocatalytic splitting of H₂O on (a) Zr-MCM-41, (b) Zr-MCM-41 (in the presence of CCl₄), (c) ZrO₂ and (d) ZrO₂ (in the presence of CCl₄).
the yield of CHCl$_3$ during the photocatalytic decomposition of CCl$_4$. On the contrary, O$_2$ yielded from the photocatalytic splitting of H$_2$O is mainly in the gaseous phase. The concentrations of O$_2$ in H$_2$O were <8 mg L$^{-1}$. It seems that in the presence of CCl$_4$, photocatalytic decomposition of H$_2$O was suppressed, which might be due to at least two possibilities: (1) $e^{-}$ needed for the 2H$^+$–H$_2$ reaction and (2) H$^+$ needed for the 2H$^+$–H$_2$ reaction was consumed in the CCl$_3$–CHCl$_3$ reaction. Since photocatalytic decomposition of CCl$_4$ might proceed via the CHCl$_3$ formation pathway, little C$_2$Cl$_2$, C$_2$Cl$_6$ or CH$_2$Cl$_2$ was found in the photocatalytic process.

4. Conclusions

Photocatalytic decomposition of CCl$_4$ (80 mg L$^{-1}$) on Zr-MCM-41 was enhanced by at least 1.96 times over that on ZrO$_2$. Photocatalytic decomposition of CCl$_4$ might proceed via a two-electron transfer process that yielded mainly CHCl$_3$, Cl$^-$ and H$_2$. Little C$_2$Cl$_2$, C$_2$Cl$_6$ or CH$_2$Cl$_2$ was found, suggesting little CHCl$_3$ involved in the secondary photocatalytic degradation process. Zr-MCM-41 also decomposed H$_2$O photocatalytically. The H$_2$ yield was about 6.5 mmol (g ZrO$_2$)$^{-1}$. About 68% of H$_2$ (6.5 mmol (g ZrO$_2$)$^{-1}$) was consumed in the formation of CHCl$_3$ in the photocatalysis process. The work reported here illustrates how photocatalytic decomposition of CCl$_4$ and H$_2$O was effected by a highly dispersed photoactive species (ZrO$_2$) in the amorphous wall of MCM-41.

Acknowledgements

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References