ELSEVIER

Photocatalytic decomposition of CCl$_4$ on Zr-MCM-41

Y.-C. Chien [a], H. Paul Wang [b,*], S.-H. Liu [c], T.L. Hsiung [b],
H.-S. Tai [d], C.-Y. Peng [b]

[a] *Department of Environmental Engineering and Science, Fooyin University, Kauhsiung County 831, Taiwan*
[b] *Department of Environmental Engineering, National Cheng Kung University, Tainan City 70101, Taiwan*
[c] *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan*
[d] *Department of Safety Health and Environmental Engineering, National Kaohsiung First University of Science and Technology, Kauhsiung County 811, Taiwan*

Abstract

Photocatalytic decomposition of CCl$_4$ (80 mg L^{-1} in H$_2$O) 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 CCl$_4$ on Zr-MCM-41 was enhanced by about 1.96 times over that on ZrO$_2$. Photocatalytic decomposition of CCl$_4$ may proceed via a two-electron transfer process that yields mainly CHCl$_3$, Cl$^-$ and H$_2$. Since little C$_2$Cl$_2$, C$_2$Cl$_6$ or CH$_2$Cl$_2$ was found, it is unlikely that CHCl$_3$ involved in the secondary photocatalytic degradation process. In addition, photocatalytic splitting of H$_2$O on Zr-MCM-41 was also enhanced. The yield of H$_2$ was 6.5 mmol (g ZrO$_2$)$^{-1}$. About 68% of this hydrogen (6.5 mmol (g ZrO$_2$)$^{-1}$) was consumed in the photocatalytic decomposition of CCl$_4$.
© 2007 Elsevier B.V. All rights reserved.

Keywords: CCl$_4$; ZrO$_2$; Zr-MCM-41; Photocatalysis

1. Introduction

CCl$_4$, a volatile organic compound (VOC), has been used as solvents in pharmaceutical, plastic, dye, oil, wax, cleaning, dry cleaning, paint and semiconductor industries [1]. CCl$_4$ with an estimated lifetime of roughly 40 years may cause depletion of stratospheric ozone [2]. It should be noted that CCl$_4$ 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 TiO$_2$ can generate strongly oxidative VB (valence band) holes and moderately reductive CB (conduction band) electrons to initiate the photocatalytic decomposition of CCl$_4$ [5,6]. ZrO$_2$ 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 m^2 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 H$_2$O 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 ZrO$_2$. Since the

reduction potential of CCl_4 (-0.51 eV) [14] is less negative than the CB of ZrO_2, photocatalytic decomposition of CCl_4 on the dispersed ZrO_2 in MCM-41 is of great interest. Thus, the aim of the work reported here was to study the photocatalytic decomposition of CCl_4 in H_2O effected by Zr-MCM-41. The reaction path in the photocatalytic decomposition of CCl_4 and H_2O has also been investigated.

2. Experimental

In the synthesis of MCM-41, fumed silica and/or sodium silicate solution (Merck) (14% NaOH and 27% SiO_2) 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 H_2O:1.0 SiO_2 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 H_2O, 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 ZrO_2 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 ZrO_2 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 CCl_4 experiments were carried out in a quartz reactor (filled with 40 mL of H_2O) with a total reflection mirror system (shown in Fig. 1). Seven and 14 mg of Zr-MCM-41 and ZrO_2 (corresponding to 192 and 350 mg ZrO_2 in 1 L of H_2O), respectively were suspended in the CCl_4 (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 CCl_4 were conducted at 400 W for at least 5 h. The intensity of the incident light to the reactor was 25 mW/cm^2 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 ^{63}Ni electron capture detector and a SUPELCO column (1% SP^{TN} 1000 support 60/80 CARBOP ACK^{TN}B 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 ZrO_2 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 (d_{100}) can be indexed on a well-defined hexagonal lattice possessing a pore diameter of about 46.7 Å. The unit cell parameter ($a_0 = 2d_{100}/\sqrt{3}$) 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 ZrO_2 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 ZrO_2 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 ZrO_2 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].
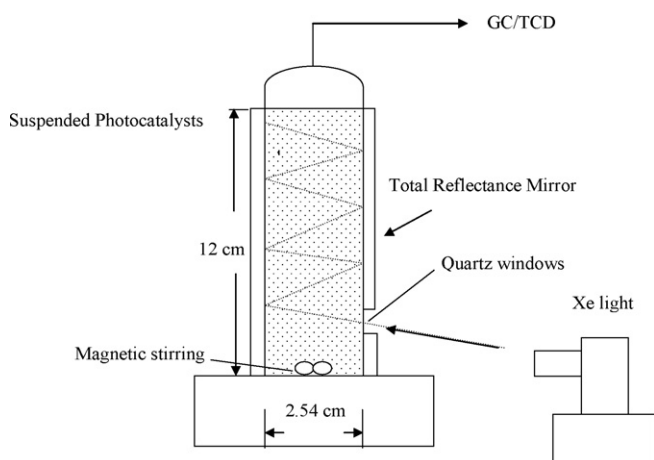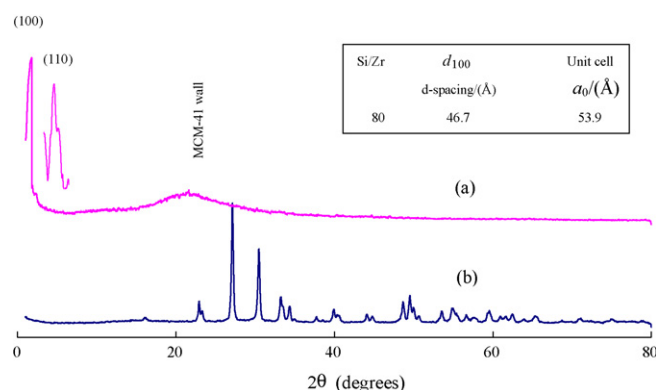

Fig. 1. Scheme of the photocatalytic reaction system.

Fig. 2. Powder X-ray diffraction patterns of (a) Zr-MCM-41 and (b) ZrO_2.

Table 1
The maximum wavelength and band gap of Zr-MCM-41 and ZrO_2 determined by UV–vis spectroscopy

Photocatalyst	Maximum wavelength (nm)	Band gap (eV)
Zr-MCM-41	208	4.92
ZrO_2	230	4.05

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

Table 2
The conversion and concentration (mmol $(g\,ZrO_2)^{-1}$) of by-products in the photocatalytic decomposition of CCl_4 (80 mg/L) on Zr-MCM-41 and ZrO_2 for 5 h irradiation

Photocatalysts	Conversion	$CHCl_3$	Cl^-	H_2	CH_2Cl_2	C_2Cl_2	C_2Cl_6
Zr-MCM-41	0.97	2.95	1.73	2.13	ND	ND	ND
ZrO_2	0.50	ND	0.80	0.21	ND	ND	ND

ND: not detectable.

The UV–vis irradiation time dependence for photocatalytic decomposition of CCl_4 (initial concentration = 80 mg L^{-1}) effected by ZrO_2 (350 mg ZrO_2 (kg $H_2O)^{-1}$) or Zr-MCM-41 (192 mg ZrO_2 (kg $H_2O)^{-1}$) is shown in Fig. 3. Without a photocatalyst, little CCl_4 was decomposed in the first 5 h. Accumulated 50% and 97% of CCl_4 was photocatalytically decomposed on ZrO_2 and Zr-MCM-41, respectively, under UV–vis irradiation for 5 h. Note that the Zr-MCM-41 possessed an enhanced photocatalytic decomposition of CCl_4 by at least 1.96 times if compared to the bulk ZrO_2. The enhancement for the photocatalytic decomposition of CCl_4 on Zr-MCM-41 may be due to at least two possibilities: (1) the high dispersion of ZrO_2 in MCM-41 may increase the number of photoactive sites and (2) the modified separation of CB electrons and VB holes of ZrO_2 moieties in MCM-41 prolongs the lifetime of photoluminescence of ZrO_2 that might alter the reaction pathways and product selectivities and enhance the electron transfer in the photocatalysis process.

Generally, photocatalytic decomposition of CCl_4 may be initiated via two possible reaction paths: (1) formation of $\cdot CCl_3$ radicals and Cl^- and (2) through a two electrons process, forming CCl_3^- and Cl^- [14–17]. Interestingly, the yield of $CHCl_3$ was about 2.95 mmol $(g\,ZrO_2)^{-1}$ in the photocatalytic decomposition of CCl_4 on Zr-MCM-41 (Table 2). Table 2 also shows that the yield of H_2 in the photocatalytic decomposition of CCl_4 on Zr-MCM-41 was about 2.1 mmol $(g\,ZrO_2)^{-1}$. The CCl_3^- may react with H^+ to form $CHCl_3$. Chio and Hoffmann reported that

trace C_2Cl_6 was found in the photocatalytic decomposition of CCl_4 without electron donors [14]. In the present work, little C_2Cl_2, C_2Cl_6 or CH_2Cl_2 was observed, suggesting little $CHCl_3$ 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 ZrO_2 (Table 2). Cl^- may be formed via the CCl_4 reduction with the CB electrons generated from the photoexcitation of ZrO_2 and Zr-MCM-41.

We also found that photocatalytic splitting of H_2O to H_2 was enhanced on Zr-MCM-41 (Fig. 4). However, H_2 was also consumed in the photocatalytic decomposition of CCl_4 (Fig. 4). The yield of H_2 was about 6.5 mmol $(g\,ZrO_2)^{-1}$ in the photocatalytic splitting of H_2O on Zr-MCM-41 for 5 h. However, only 2.1 mmol H_2 $(g\,ZrO_2)^{-1}$ were yielded from the photocatalytic decomposition of CCl_4 on Zr-MCM-41. A possible mechanism for photocatalytic decomposition of CCl_4 effected by the suspended Zr-MCM-41 in H_2O is shown in Scheme 1. Photoexcitation of the Zr-MCM-41 generated oxidative VB holes and reductive CB electrons. The photocatalytic decomposition of CCl_4 may be initiated by two-electron process to form CCl_3^- 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 H_2O. Apparently, CCl_3^- reacted with H^+ to form $CHCl_3$. Stoichiometrically, 68% of H_2 was consumed in
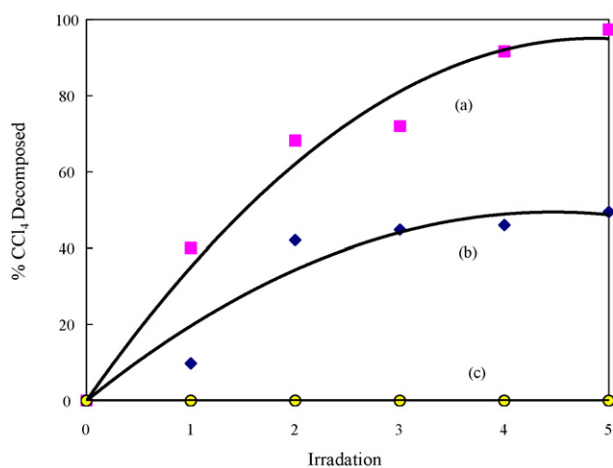

Fig. 3. Irradiation time dependence for the photocatalytic decomposition of CCl_4 (80 mg L^{-1} in H_2O) effected by (a) Zr-MCM-41 (192 mg ZrO_2 (kg $H_2O)^{-1}$) and (b) ZrO_2 (350 mg ZrO_2 (kg $H_2O)^{-1}$) and (c) without a catalyst.
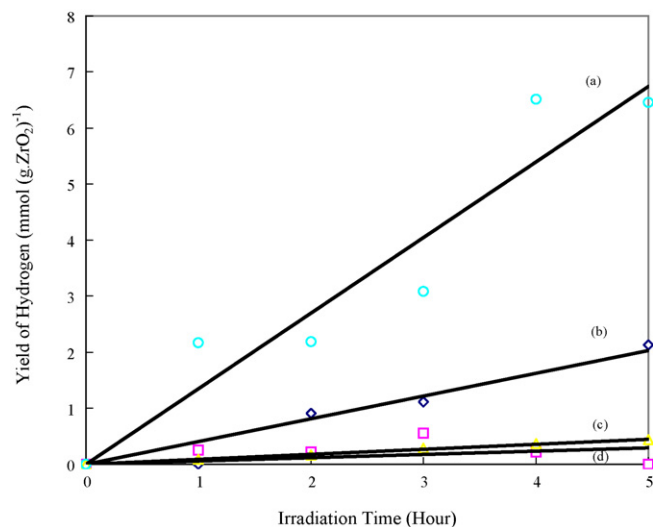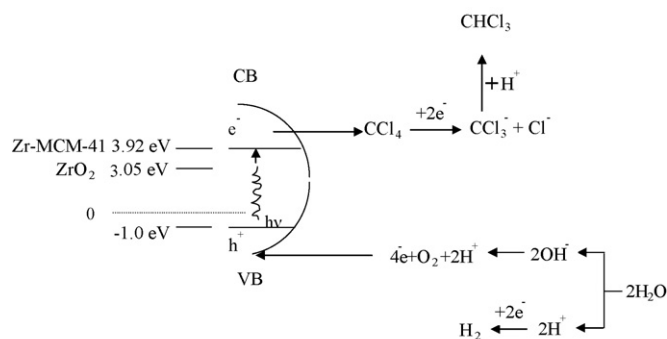

Fig. 4. The yield of H_2 (mmol $(g\,ZrO_2)^{-1}$) in the photocatalytic splitting of H_2O on (a) Zr-MCM-41, (b) Zr-MCM-41 (in the presence of CCl_4), (c) ZrO_2 and (d) ZrO_2 (in the presence of CCl_4).

Scheme 1.

the yield of $CHCl_3$ during the photocatalytic decomposition of CCl_4. On the contrary, O_2 yielded from the photocatalytic splitting of H_2O is mainly in the gaseous phase. The concentrations of O_2 in H_2O were <8 mg L^{-1}. It seems that in the presence of CCl_4, photocatalytic decomposition of H_2O 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_2Cl_2, C_2Cl_6 or CH_2Cl_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_2Cl_2, C_2Cl_6 or CH_2Cl_2 was found, suggesting little $CHCl_3$ involved in the secondary photocatalytic degradation process. Zr-MCM-41 also decomposed H_2O 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_2O was effected by a highly dispersed photoactive species (ZrO_2) in the amorphous wall of MCM-41.

Acknowledgements

References

[1] M. Xieqi, B. Cicek, S.M. Senkan, Chemical structures of fuel-rich and fuel-lean flames of CCl_4/CH_4 mixtures, Combust. Flame 94 (1993) 131–145.

[2] P.G. Simmonds, D.M. Cunnold, R.F. Weiss, R.G. Prinn, P.J. Fraser, A. McCulloch, F.N. Alyea, S. O'Doherty, Global trends and emission of CCl4 from in situ background observations from July 1978 to June 1996, J. Geophys. Res. 103 (1998) 16017–16027.

[3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental application of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.

[4] D.F. Ollis, E. Pelizzetti, N. Serpone, Photocatalyzed destruction of water contaminants, Environ. Sci. Technol. 25 (1991) 1522–1529.

[5] C.Y. Hsiso, C.L. Lee, D.F. Ollis, Heterogeneous photocatclysis: degradation of dilute solutions of dichloromethane ($CHCl_2$), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) with illuminated TiO_2 photocatalyst, J. Catal. 82 (1983) 418–423.

[6] A.L. Pruden, D.F. Ollis, Degradation of chloroform by photoassisted heterogeneous catcaysis in dilute aqueous suspensions of titanium dioxide, Environ. Sci. Technol. 17 (1983) 628–631.

[7] K. Sayama, H. Arakawa, Photocatalytic decomposition of water and photocatalytic reduction of carbon dioxide over ZrO_2 catalyst, J. Phys. Chem. 97 (1993) 531–533.

[8] K.M. Ganguly, S. Sarkar, S.N. Bhattacharyya, Zirconum dioxide: a new photosensitizer under UV irradiation, J. Chem. Soc. Chem. Commun. (1993) 682–683.

[9] C.T. Kreseg, M.E. Leonowcz, W.J. Roth, J.C. Vartuli, J.S. Beck, Ordered mesoporous molecular sieves synthesized by a liquid–crystal template mechanism, Nature 359 (1992) 710–712.

[10] R. Schmidt, E.W. Hansen, M. Stöcker, D. Akporiaye, O.H. Ellestad, Pore size determination of MCM-41 mesoporous materials by means of ^{1}H NMR spectroscopy, N_2 adsorption, and HREM. a preliminary study, J. Am. Chem. Soc. 117 (1995) 4049–4056.

[11] S.G. Zhang, Y. Fujii, H. Yamashita, K. Koyano, T. Tatsumi, M. Anpo, Photocatalytic reduction of CO_2 with H_2O on Ti-MCM-41 and Ti-MCM-48 mesoporous zeolites at 328 K, Chem. Lett. (1997) 659–660.

[12] S.H. Liu, H.P. Wang, N.B. Chang, K.S. Lin, Y.S. Chen, M.C. Hsiao, W.H. Tuen, Photodecomposition of H_2O catalyzed by Zr- and Ti-MCM-41, Energ. Sources 25 (2003) 591–596.

[13] S.H. Liu, H. Paul Wang, Photocatalytic generation of hydrogen on Zr-MCM-41, Int. J. Hydrogen Energy 27 (2002) 859–862.

[14] W. Choi, M.R. Hoffmann, Photoreductive mechanism of CCl_4 degradation on TiO_2 particles and effects of electron donors, Environ. Sci. Technol. 29 (1995) 1646–1654.

[15] B.A. Balko, P.G. Tratnyek, Photoeffects on the reduction of carbon tetrachloride by zero-valent iron, J. Phys. Chem. B 102 (1998) 1459–1465.

[16] P. Calza, C. Minero, E. Pelizzetti, Photocatalytically assisted hydrolysis of chlorinated methanes under anaerobic conditions, Environ. Sci. Technol. 31 (1997) 2198–2203.

[17] M. Hirokazu, Y. Hiroshi, Photochemical properties of iron oxide incorporated in clay interlayers, J. Chem. Soc., Faraday Trans. L. 85 (1989) 1873–1880.