ChemComm
www.rsc.org/chemcomm

# Magnetic field effect on photocatalytic degradation of benzene over Pt/TiO$_2$

**Wen Zhang, Xuxu Wang and Xianzhi Fu***
*Research Institute of Photocatalysis, College of Chemistry & Chemical Engineering, Fuzhou University, Fuzhou 350002, P. R. China. E-mail: xzfu@fzu.edu.cn; Fax: +86-591-3738608; Tel: +86-591-3738608*

*Received (in Cambridge, UK) 15th May 2003, Accepted 15th July 2003*
*First published as an Advance Article on the web 24th July 2003*

**The magnetic field effect on heterogeneous photocatalytic degradation of benzene over Pt/TiO$_2$ has been observed for the first time. The coupling effect between magnetic field and photo field influences the conversion of benzene and production of CO$_2$ in different modes.**

After the discovery of nuclear and electronic spin polarization phenomena during chemical reactions (CIDNP, CIDEP), the study of magnetic field effects on the kinetics of chemical reactions, especially the free radical-involved reactions, has achieved significant accomplishment.[1–5] However, there is less study concerning the effect of magnetic field on heterogeneous photocatalytic reactions. Actually, in the presence of O$_2$, the common characteristic of all photocatalytic degradation reactions is the generation of extraordinarily reactive free radicals and radical ions such as $O_2^{-\cdot}$, $O_2^{\cdot}$, $HO_2^{\cdot}$, $OH^{\cdot}$ and so on.[6] So it is reasonable to consider that the behaviour of the photo-induced electrons and holes, together with the radicals and radical ions produced, may be affected by magnetic field.

Here we report the magnetic field effect on the heterogeneous photocatalytic degradation of benzene over Pt/TiO$_2$. Titanium dioxide xerogel having diameters of 0.2 and 0.3 mm were prepared by a sol–gel technique that involved the controlled hydrolysis of titanium tetraisopropoxide followed by dialysis to pH = 4, evaporating of the solvent at 60 °C, grinding and sieving.[7] Platinized titania (Pt/TiO$_2$) particles were synthesized by impregnating the TiO$_2$ xerogel prepared as above with an aqueous H$_2$PtCl$_6$ solution. The adsorbed H$_2$PtCl$_6$ was then reduced with a solution of 0.1 M sodium borohydride in 0.1 M NaOH.[8] The resulting sample was dried at 110 °C and then calcinated at 300 °C for 3 h with a temperature ramping of 2 °C per minute. The Pt/TiO$_2$ catalyst employed for this study contained 0.5% Pt by weight. The dominant crystal phase was anatase (79%) with average crystal size of 10.4 nm. Specific surface area of the platinized titania particles was *ca.* 124 m$^2$ g$^{-1}$.

Photocatalytic experiments were conducted in a fixed bed cylindrical photoreactor operated in a single-pass mode. The catalyst (0.4 g) was loaded in a quartz tube, which was surrounded by an electromagnetic device with the magnetic field direction vertical to the axes of the reactor tube and by four 4W ultraviolet lamps with a wavelength centered at 254 nm. The magnetic field intensity was controlled with a transformer. The reaction temperature was maintained at 65 °C.

Benzene at a concentration of 230 ppm with a balance of zero air was supplied to the system without further purification. The flow rate was kept at 20 ml min$^{-1}$. Simultaneous determination of benzene and CO$_2$ concentration was performed with an on-line gas chromatograph (HP6890, Porapak R) equipped with a flame ionization detector and a thermal conductivity detector.

Fig. 1 and Fig. 2 showed the influence of magnetic field on conversion of benzene and production of CO$_2$ for the photocatalytic degradation of benzene over Pt/TiO$_2$, respectively. When the photocatalytic reaction without external magnetic field reached the steady state, the conversion of benzene was 15.5% (Fig. 1), and the production of CO$_2$ was 52 ppm (Fig. 2). Then an external magnetic field (59.42mT) was applied on the reaction system. The conversion of benzene reached 18% (Fig. 1), which was slightly larger than that obtained for the reaction without magnetic field, and the production of CO$_2$ was rapidly increased to 175 ppm (Fig. 2). Accordingly, the mineralization of benzene was up to 52% from 19%. After 840 minutes, the electromagnetic field was turned off. Conversion of benzene decreased rapidly and became *ca.* 4%. At the same time, the formation of CO$_2$ also decreased dramatically and resumed the low values obtained before application of the magnetic field. A subsequent reapplication of the magnetic field (from 1500 minutes) led to recovery of most of the photocatalytic activity.

Experiments performed in the absence of UV light or catalyst confirmed that no reaction occurred under these conditions, with or without magnetic field. Moreover, the results of UV-vis diffuse reflection spectra indicated that the external magnetic field has no effect on photoabsorption of the Pt/TiO$_2$ catalyst. In addition, there was no magnetic field effect over the pure TiO$_2$ photocatalyst because of the serious deactivation for the reaction over TiO$_2$ photocatalyst.[9] This result implied that the

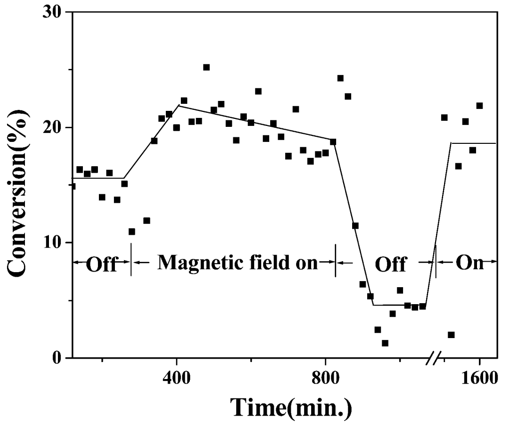

**Fig. 1** Effect of magnetic field on the photocatalytic conversion of benzene.

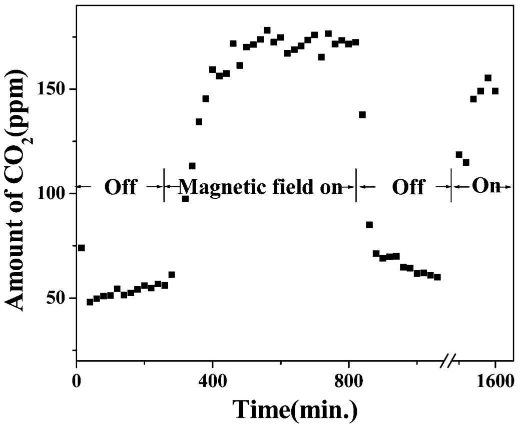

**Fig. 2** Effect of magnetic field on CO$_2$ yield for photocatalytic degradation of benzene.

DOI: 10.1039/b305460h

magnetic field effect is related to the existence of Pt. By contrast, in a similar experiment which was conducted with the magnetic field turned on and fresh Pt/$TiO_2$ catalyst, no remarkable magnetic field effect was observed. The conversion of benzene for this experiment was only slightly higher than the initial conversion shown in Fig. 1. After that, the magnetic field was turned off, and then the same experiment as in Fig. 1 was conducted. A similar result as in Fig. 1 was obtained. Comparing the above results with those of Fig. 1 and Fig. 2 suggests that the magnetic field effect may be related to an acceleration of oxidative decomposition of intermediate species on the loaded platinum.

Indeed, the carbon mass balance was not perfect in the initial period of photocatalytic degradation (Fig. 1 and Fig. 2). It may be ascribed to the formation and deposition of some polymeric compounds or coke on the catalyst surface.[10] In the second period of photocatalytic degradation under magnetic field, improvements to the conversion of benzene and the oxidation selectivity to $CO_2$ were achieved. Although the detailed mechanism of the magnetic field effect is still unknown at present, there is a possible explanation for the improvements on the basis of the above experimental results. That is, the chemical and electronic states of highly dispersed Pt atoms on the surface of the catalyst were changed by applying the magnetic field, leading to accelerated decomposition of reaction intermediates deposited on the surface of Pt/$TiO_2$ catalyst.

Fig. 3 shows the photocatalytic activity as a function of magnetic field intensity. The benzene conversion and the production of $CO_2$ are measured at steady state. Three regions are presented in the diagram. In the first region (**a**) from zero to 23 mT, the conversion decreased with increasing magnetic field intensity. The conversion reached a minimum (about 4.5%) at 23 mT. Over the second regime (**b**) between 23 mT to 52 mT, the conversion returned to the value (14.8%) obtained in the absence of an applied magnetic field. The conversion then rapidly increased with further increase in magnetic field intensity. These results indicate that the photocatalytic conversion of benzene was suppressed under the low magnetic field intensity, and was promoted at the higher magnetic field intensity. However, the effect of the magnetic field on the production of $CO_2$ was positive over the whole intensity range employed. The reason for the phenomena is still unknown. Further studies on the detailed mechanism of the magnetic field effect on heterogeneous photcatalytic reaction are in progress in our laboratory.

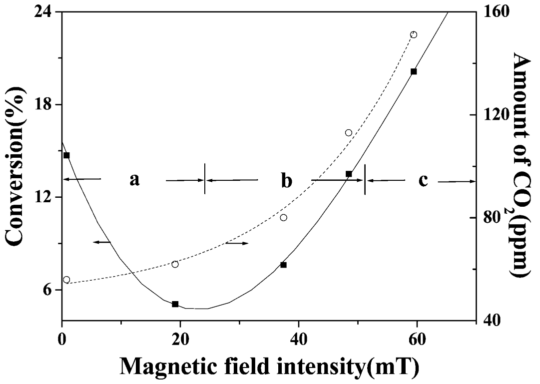

Fig. 3 Magnetic field intensity dependence of conversion (■) and $CO_2$ yield (○).

This work was supported financially by the National Natural Science Foundation of China (No. 20133010).

## Notes and references

1 U. E. Steiner and T. Ulrich, *Chem. Rev.*, 1989, **89**, 51–147.
2 S. Maiti and D. Bag, *Indian J. Chem.*, 1995, **34A**, 673–687.
3 B. Brocklehurst, *Chem. Soc. Rev.*, 2002, **31**, 301–311.
4 J. R. Woodward, C. R. Timmel, P. J. Hore and K. A. Mclauchlan, *Riken Rev.*, 2002, **44**, 79–81.
5 H. Hayashi, Y. Sakaguchi and M. Wakasa, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 773–783.
6 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnmann, *Chem. Rev.*, 1995, **95**, 69–96.
7 Q. Xu and M. A. Anderson, *J. Mater. Res.*, 1991, **6**, 1073–1081.
8 S. Sato, *J. Catal.*, 1985, **92**, 11–16.
9 The $TiO_2$ catalyst was prepared by calcinating the xerogel at 300 °C for 3 h.
10 S. Sitkiewitz and A. Heller, *New J. Chem.*, 1996, **20**, 233.