

***In situ* FTIR Investigation of Magnetic Field Effect on Heterogeneous Photocatalytic Degradation of Benzene over Pt/TiO₂**

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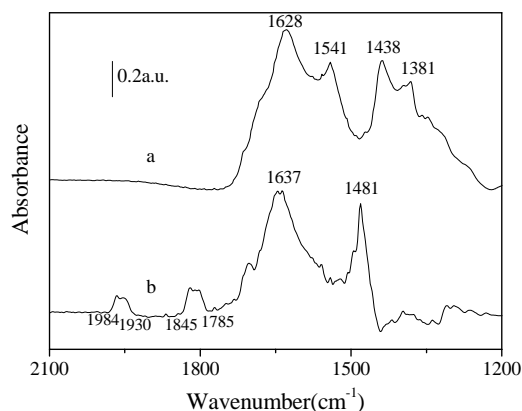
Abstract: *In situ* FTIR spectroscopy was utilized to investigate the magnetic field effect on the heterogeneous photocatalytic degradation of benzene over platinized titania (Pt/TiO₂). The results revealed that the employment of magnetic field may not change the mechanism of photocatalytic degradation of benzene, however, it greatly facilitate the conversion of benzene to phenol and quinone, as well as the transformation from phenol to quinone, resulting in opening the benzene ring easily and promoting the production of CO₂.

Keywords: *In situ* FTIR, magnetic field effect, photocatalytic degradation, Pt/TiO₂.

Recently, we published a remarkable effect of magnetic field (MF) on the photocatalytic degradation of benzene over Pt/TiO₂¹. In this paper, we applied *in-situ* FTIR spectroscopy to identify the difference of intermediates on the surface of irradiated Pt/TiO₂ during the reaction in the absence or presence of magnetic field.

The FTIR measurement was carried out in a single-pass mode, simulating the experimental conditions during the photocatalytic reactivity tests¹. Platinized titania (Pt/TiO₂) was prepared as the methods in the reference¹. Benzene gas (molar fraction: 3.5×10⁻²) was introduced into the IR cell, the highly purified O₂ was passed through the benzene saturator, which was placed in a ice water bath, and the flow rate of benzene gas was kept at 30 mL·min⁻¹. A novel *in-situ* FTIR reaction cell was composed of a quartz cell, CaF₂ windows, and a teflon sample holder. The radiation (maximal emission at 365 nm) with UV/Vis source of a 250 W mercury lamp was fed to the reactor by a fiber optic light-guide. The two blocks of permanent magnet were easily removed in the condition without magnetic field. For the IR measurements, the catalyst was pressed in the form of wafer and the typical density was *ca.* 10-12 mg·cm⁻². The IR spectra between 4000 cm⁻¹ and 1100 cm⁻¹ (32 scans and 4 cm⁻¹ resolution) were recorded in the transmission mode with a Nicolet Nexus 670-FTIR equipped with a DTGS-KBr detector. A background FTIR spectrum was obtained, when the cell was evacuated by both mechanical and turbomolecular pumps (residual pressure: 1×10⁻³ Pa) at ambient temperature.

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Figure 1 FTIR spectra (2100-1200 cm^{-1}) of the Pt/TiO₂ catalysts

(a) after pre-outgassed for 40 min and (b) adsorption of benzene at room temperature.

Figure 1b showed the typical benzene adsorption bands at 1481 cm^{-1} , 1984-1930 cm^{-1} and 1845-1785 cm^{-1} , as benzene got adsorption equilibrium over Pt/TiO₂ at room temperature. To compare the spectral characteristics of the wafer before and after the adsorption of benzene, the spectra of fresh catalyst surface after evacuation for 40 minutes (**Figure 1a**) is also shown as reference.

According to the UV absorption spectra, benzene absorbed at wavelength below 256 nm. So, it is reasonable to deem that the UV light may not cause direct photolysis of benzene.

When benzene got adsorption equilibrium on the surface of the catalyst, the wafer was irradiated with UV light. Increase of the irradiation time caused gradual increase in the intensity of characteristic peaks of CO₂ (2389-2283 cm^{-1}) and decrease of benzene (1984-1930 cm^{-1}). After 180 minutes of irradiation, the steady-state conversion of benzene was achieved, no more change of the amount of benzene and CO₂ was observed. Then an external magnetic field was applied to the photoreaction IR cell, the intensity of CO₂ and benzene continued to increase and decrease sharply, indicating that the conversion and mineralization of benzene were improved by magnetic field.

Figure 2 illuminated the magnetic field effect on the photocatalytic degradation of benzene quantitatively. The integration range for benzene was 1984-1930 cm^{-1} , and for CO₂ was 2389-2283 cm^{-1} . When the photocatalytic reaction reached the steady state, the integration area of benzene was 0.82, and CO₂ was 28.3. When external magnetic field was employed to the reaction, the amount of benzene and CO₂ kept decreasing and increasing, respectively. These results were in agreement with our previous photocatalytic reactivity tests¹. When the magnetic field was applied to the benzene degradation system, the reaction mechanism might be changed or the decomposition of the intermediates deposited on the surface of Pt/TiO₂ might be accelerated during the reaction.

Figure 2 Magnetic field effect on the IR integrated area of benzene (○) and CO₂ (●)

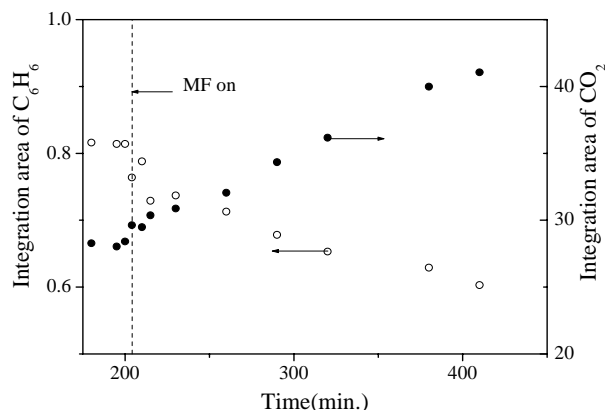
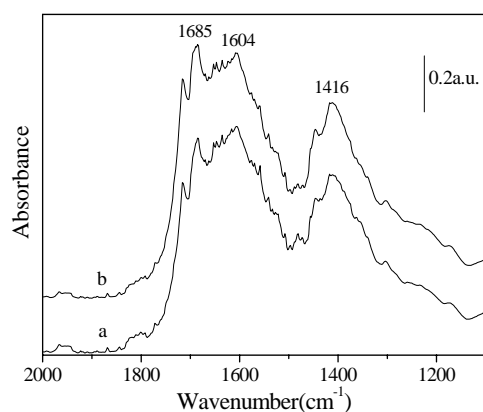


Figure 3 FTIR spectra of the samples



a: photocatalytic reaction at steady state; b: after 210 min MF applied.

To clarify the magnetic field effect on the intermediates produced during the photocatalytic degradation process, **Figure 3** showed the difference before and after the employment of magnetic field at region 2000-1100 cm⁻¹. As previously reported², phenol and quinone are two major possible surface intermediates generated during the photocatalytic oxidation of benzene over TiO₂. From the spectra, we noted that there was no appearance of new peak and the peak position of the intermediates almost remained unchanged in the condition without and with the external magnetic field despite of the different intensity. The peak at 1604 cm⁻¹ could be attributed to the ring stretching of benzene derivatives, like phenol, being overlapped with those for the adsorbed water and/or hydroxyl groups³. At the same time, the band at 1416 cm⁻¹ due to the O-H in-plane bending vibration of phenol was also observed⁴. The band at 1685 cm⁻¹ was ascribed to the carbonyl (C=O) stretching vibration of quinone³. These results suggested that phenol and quinone are still two potential intermediates produced during the reaction over Pt/TiO₂. Moreover, the results also implied that the application of

magnetic field might not change the reaction route of the photocatalytic degradation of benzene.

As shown in **Figure 3a**, when the photocatalytic reaction got its steady state, the intensity of the peaks at 1685 and 1604 cm^{-1} were 0.725 and 0.756, respectively. After the employment of the magnetic field for 210 minutes, the intensity of the two peaks increased to 0.860 and 0.819 (**Figure 3b**). Accordingly, the relative intensity of the former peak to the latter one was up to 1.05 from 0.96. These results implied that the application of external magnetic field not only favor the conversion of benzene, leading to the increase of phenol and quinone, but also facilitate the conversion of phenol to quinone, opening the benzene ring became easier and the amount of CO_2 increased (**Figure 2**). That means, the application of magnetic field changed the distribution of the intermediates and product, improved the performance of the photocatalytic degradation.

Acknowledgments

This work was supported financially by the National Natural Science Foundation of China (No. 20133010) and Education Department of Fujian (No. JB04238).

References

1. W. Zhang, X. Wang, and X. Fu, *Chem. Commun.*, **2003**, 2196.
2. W. Jacoby, D.M. Blake, J.A. Fennell, *et al.*, *J. Air & Waste Magene. Assoc.*, **1996**, *46*, 891.
3. H. Einaga, S. Futamura and T. Ibusuki, *Phys. Chem. Chem. Phys.*, **1999**, *1*, 4903.
4. J. Wu, *Modern Technology and Application of Fourier Transform Infrared Spectrometry*(in Chinese), Sci. Tech. Lit. Press, **1994**.

Received 12 November, 2004