H$_2$–O$_2$ atmosphere increases the activity of Pt/TiO$_2$ for benzene photocatalytic oxidation by two orders of magnitude†

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Unprecedented photocatalytic activity and durability of Pt/TiO$_2$ for decomposing persistent organic pollutants (*e.g.* benzene) have been obtained by adding trace H$_2$ into an O$_2$-rich photooxidation system.

Benzene and its derivatives (*e.g.* toluene and xylene) are widespread environmental pollutants commonly found in groundwater, soil and air. Because of their high toxicity and confirmed carcinogenicity, as well as their environmental persistence, they are regarded as priority hazardous substances for which efficient treatment technologies are needed.[1]

TiO$_2$-based photocatalytic oxidation (PCO) is established to be one of the most promising technologies for environmental pollutant remediation. However, our previous studies showed that the photocatalysts (typically, TiO$_2$ and Pt/TiO$_2$) suffer from the limitations of low activity and poor durability during the treatment of stable aromatic compounds such as benzene.[2,3] Although the photocatalytic activity of Pt/TiO$_2$ for benzene degradation has recently been improved by applying a magnetic field to the C$_6$H$_6$–O$_2$–Pt/TiO$_2$ photocatalytic system,[4] the efficiency of the magnet-assisted photocatalysis is still relatively low for practical application. In this work, a more promising strategy was developed to greatly enhance the performances of Pt/TiO$_2$ for benzene photocatalytic oxidation. In this strategy, hydrogen gas was introduced into the O$_2$-rich photooxidation system for improving photocatalytic performances. It is well-known that both H$_2$ and O$_2$ can dissociatively adsorb on the surface of Pt particles to give O and H adatoms.[5] These active surface O and H adatoms would serve as effective trapping centers for photoinduced electron and hole, respectively, and thus, prohibiting photocarrier recombination. Therefore, a significant increase in the photocatalytic quantum efficiency of Pt/TiO$_2$ can be attained.

Pure TiO$_2$ samples were prepared by calcining the sol–gel-derived xerogel at 623 K for 6 h.[6] The Pt/TiO$_2$ was prepared by impregnating the calcined TiO$_2$ with an aqueous solution of H$_2$PtCl$_6$. The impregnated sample was dried at 383 K, and then calcined at 623 K for 3 h. The sample thus obtained was subsequently reduced with a NaBH$_4$ solution (0.1 M) to produce Pt/TiO$_2$.[2] The initial ratio of Pt to TiO$_2$ was fixed at 1 wt.%.

The photocatalytic reactivity measurement was carried out in a fixed-bed reactor operated at atmospheric pressure. The reactor was a 11 cm long 2.4 mm diameter quartz tube surrounded by four 4 W UV-lamps with a wavelength centered at 254 nm (Philips, TUV 4W/G4 T5). Benzene (845 ppm) bubbled with oxygen and 7.8% hydrogen in nitrogen was fed to 0.05 g of catalyst at a total flow-rate of 50 cm^3 min^{-1}. The effluent gas was analyzed by an online gas chromatograph (HP6890). The temperature of reactions was controlled at 303 ± 1 K by an air-cooling system.

Fig. 1 shows the photocatalytic conversion of benzene over Pt/TiO$_2$ under different atmospheres. Obviously, under H$_2$ or pure O$_2$ atmosphere, the conversion of benzene is negligibly small. In the case of H$_2$ gas, the conversion of benzene is about zero. Beyond this, neither hydrogenation products (*e.g.* cyclohexane and

cyclohexene) nor CO$_2$ is detected. These results suggest that both photocatalytic oxidation and hydrogenation reactions do not occur in the presence of H$_2$ gas. This is expected because the PCO of benzene usually requires oxygen molecules and the thermally catalytic hydrogenation of benzene occurs at higher temperatures.[7] When the experiment is conducted in pure O$_2$ atmosphere, initially, the benzene conversion is 16%; but it decreases significantly to 3% after PCO for 2 h. Meanwhile, no detectable CO$_2$ is observed. These indicate that only a small amount of benzene is partially oxidized. This decrease in the conversion is attributed to the fact that the intermediates of benzene photocatalytic degradation occupied the active sites and deactivated the catalyst.[2,8] Interestingly, when the feeding gas contains both H$_2$ and O$_2$, the photocatalytic performance of Pt/TiO$_2$ dramatically enhances. The conversion of benzene increases up to 71%, accompanied by producing a large amount of CO$_2$. The CO$_2$ yield is calibrated to be 2853 ppm (see Fig. 2), corresponding to a benzene mineralization ratio ([CO$_2$]$_{produced}$/[C$_6$H$_6$]$_{converted}$) of 4.7. Such a high photocatalytic activity and a mineralization ratio can be maintained for more than 48 h.

Fig. 2 shows the benzene photocatalytic conversion and mineralization ratios as functions of the H$_2$/O$_2$ ratio. The conversion of benzene and the production of CO$_2$ are measured at steady state after PCO for 6 h. The result shows that the photocatalytic conversion and mineralization ratio of benzene can be improved even in trace amount of H$_2$, and are sensitive to the H$_2$/O$_2$ ratio. When the H$_2$/O$_2$ ratio increases from 0 to 0.05, the photocatalytic conversion of benzene increases rapidly from 3% to 93%. Further increasing H$_2$/O$_2$ ratio from 0.05 to 0.31, the conversion steadily increases from 93% to 100% with a slower increasing rate. It should be noted that the complete mineralization of benzene to CO$_2$ and H$_2$O can be achieved when the H$_2$/O$_2$ ratio is 0.31. However, when the H$_2$/O$_2$ ratio is further increased to a higher value than 0.31, a significant drop of both conversion and mineralization ratios occurs. It is not surprising that too high a H$_2$/O$_2$ ratio is disadvantageous to the complete degradation of
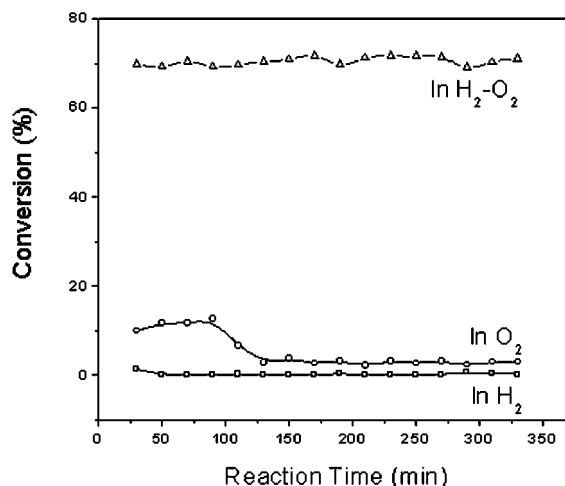

Fig. 1 Effect of different reaction atmospheres on the conversion of benzene over Pt/TiO$_2$ photocatalyst. (H$_2$/O$_2$ ratio: 0.02).

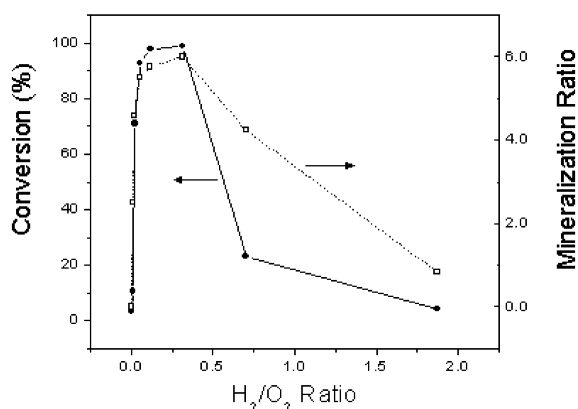† Electronic supplementary information (ESI) available: Plots of photocatalytic oxidation conversion and EPR spectra. See http://www.rsc.org/suppdata/cc/b4/b408187k/

Fig. 2 Effect of H_2/O_2 ratio on the photocatalytic performance of Pt/TiO_2 toward benzene decomposition.

benzene, because the oxidation of benzene stoichiometrically requires a large amount of O_2, and therefore, the presence of excess H_2 is unfavourable for the reaction.
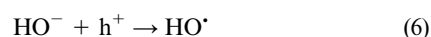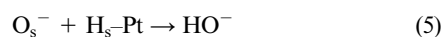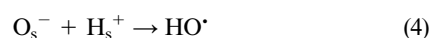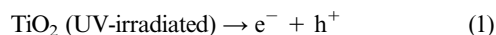
As a comparison, we also measured the photocatalytic performances of pure TiO_2 and Pt (deposited on an insulator such as silica) under the same experimental conditions (H_2/O_2 ratio: 0.02). As expected, either TiO_2 or Pt alone shows poor catalytic performances toward benzene photooxidation. After PCO for 6 h, no detectable benzene degradation was observed (Fig. S1 of the ESI†). It is therefore believed that the interactions among TiO_2, Pt, H_2 and O_2 contribute to the superior activity and durability of Pt/TiO_2 for benzene photodecomposition.

The proposed photochemical processes in the H_2–O_2–Pt/TiO_2 reaction system are elucidated in Scheme 1 and eqns. (1)–(6). These processes may involve several steps: (a) O_2 and H_2 dissociatively adsorb on Pt particles to give surface O (O_s) and surface H (H_s) adatoms. (b) the resulting O_s adatom captures photogenerated electron form Pt particles, producing the O_s^- ion. (c) the H_s adatom migrates (spills over) from Pt to the interface of Pt‖TiO_2,[9] and then servers as trapping agent for the hole, generating a surface proton (H_s^+) which further reacts with the O_s^- ion to give highly active $HO^{\bullet}$ group. (d) the O_s^- ion could also react with the H_s adatom to produce HO^- group that also captures h^+, leading to the formation of $HO^{\bullet}$ radicals. These four processes are believed to generate a large amount of $HO^{\bullet}$ radicals, which is proved by the electron paramagnetic resonance spectra (EPR) (Fig. S2 of the ESI†). Since the oxidative degradation of benzene is initiated by $HO^{\bullet}$,[10] a large increase in the photocatalytic activity is possible. As the excess H_2 would consume the produced hydroxyl radicals (eqn (7)), this results in the consequent decrease in the conversion (Fig. 2). Although eqn (8) may also produce $HO^{\bullet}$ radicals,[11] we found that this non-photogenerated $HO^{\bullet}$ has only slight effect on the overall catalytic performance, as revealed by the oxidation of
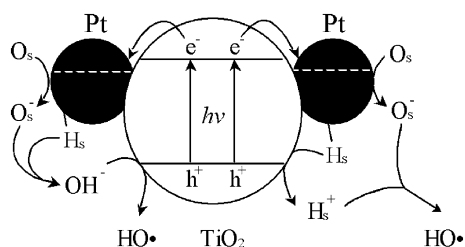
Scheme 1 Proposed mechanism for the photochemical generation of $HO^{\bullet}$ radical on Pt/TiO_2 catalyst in the coexistence of H_2 and O_2.

benzene on Pt/TiO_2 in the dark (Fig. S3 of the ESI†).

$$TiO_2 \text{ (UV-irradiated)} \rightarrow e^- + h^+ \quad (1)$$

$$O_s\text{–Pt} + e^- \rightarrow O_s^- \quad (2)$$

$$H_s\text{–Pt} + h^+ \rightarrow H_s^+ \quad (3)$$

$$O_s^- + H_s^+ \rightarrow HO^{\bullet} \quad (4)$$

$$O_s^- + H_s\text{–Pt} \rightarrow HO^- \quad (5)$$

$$HO^- + h^+ \rightarrow HO^{\bullet} \quad (6)$$

$$H_s + HO^{\bullet} \rightarrow H_2O \quad (7)$$

$$O_s\text{–Pt} + H_s\text{–Pt} \rightarrow HO^{\bullet} \quad (8)$$

Moreover, owning to its small size and high mobility, the H adatom may significantly perturb the metal surface structure inducing reconstruction/cleaning of the metal surface.[12] This might contribute to the long catalytic lifetime of Pt/TiO_2.

Furthermore, it is noted that the interfacial electron-transfer on photocatalyst surface is a rate-determining step during the photocatalytic reactions.[13] Normally, the interfacial electron-transfer is accomplished by trapping the electron at surface-adsorbed O_2.[13] As the electron-affinity of O_2 (O_2/O_2^-, 0.43 eV) is much lower than that of O adatom (O/O^-, 1.478 eV),[14,15] the O adatom should be a superior trapping agent for the electron (eqn. (1)), as compared with O_2. Subsequent capturing of the resulting O_s^- ion by H_s^+/H_s (eqns. (4) and (5)) could further favor the interfacial electron transfer. An increase in the interfacial electron-transfer rate is expected to result in higher quantum efficiencies for the photocatalytic reactions.

Notes and references

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