CO_2 Sequestration and Recycle by Photosynthesis

Technical Progress Report

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ABSTRACT

Hydrocarbon oxygenate synthesis from photocatalytic reactions of CO_2 and H_2O over various catalysts is a very attractive process. However, the formation rate of the hydrocarbons and oxygenates is significantly lower than conventional catalysis. One possible reason for the low rate of product formation is the presence of oxidation sites which reoxidize the products back to OO_2 and H_2O. For further improvement of catalytic activity for the reduction process, it is essential to understand the oxidation reaction process. We have studied photocatalytic oxidation of methylene blue and found the oxidation rate is significantly higher than the reduction rate.

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INTRODUCTION

TiO_2 is the most widely studied photocatalyst because of its stability, low cost, and non-toxicity. TiO_2 exhibits the photocatalytic activity for both oxidation and reduction. Photocatalytic oxidation usual involves oxidation of organic species to CO and H_2O in the presence of H_2O or O_2 while photocatalytic reduction converts CO_2/H_2O back to hydrocarbons/oxygenates or reduces H_2O to H_2 and O_2. Examination of literature results shows that the rates of photocatalytic reduction are 3 to 4 orders of magnitude lower than those of photocatalytic oxidation. Significant enhancement in the rate of photocatalytic reduction is needed to bring this reaction process for practical applications.

One possible reason for the low rate of the photocatalytic reduction is the presence of oxidation sites on the TiO_2 surface which further converts hydrocarbon/oxygenate products back to CO_2 and H_2O. A fundamental understanding of the reaction mechanism could assist in identifying key factors in improving Ti-based catalysts for controlling photocatalytic oxidation and reduction. To develop a better understanding of photocatalytic oxidation, we have studied photocatalytic oxidation of methylene blue (MB). MB is an excellent model compound for investigation of photocatalytic oxidation mechanism for (i) easy of determination of it conversion with UV-vis spectrophotometry and (ii) existence of abundant rate data for comparison.

EXECUTIVE SUMMARY

This study shows that the photocatalytic oxidation activity of TiO_2 – based catalysts is significantly higher than their photocatalytic reduction rate. Selective inhibition of photocatalytic oxidation is needed to improve the overall rate of the photocatalytic reduction

process.

EXPERIMENTAL

TiO_2 was supplied by Degussa (P-25, surface area ~50 m^2/g; mean diameter ca. 30 nm; 80% anatase and 20% rutile); Methylene Blue ($C_{16}H_{18}ClN_3S•3H_2O$) from Alfa Aesar. Both compounds were used without further treatment.

Catalyst Preparation and Characterization

0.5 wt % Pt/TiO_2 was prepared by photo-reduction of K_2PtCl_6 onto TiO_2 in a solution containing ethanol which serves as a sacrificial electron donor. The specific procedure involves (i) bubbling N_2 through a 0.1 M ethanol solution containing K_2PtCl_6 and TiO_2 particles to remove O_2, (ii) illuminating the solution with a 350 W mercury UV lamp (Oriel 6286) for 24 hours while suspending TiO_2 particle in the solution by magnetic bar stirring, (iii) removal of Pt/TiO_2 from the solution by centrifuging, (iv) washing the particle with deionized water to remove Cl and K ion, (v) and drying under vacuum oven at 100 $^{\circ}C$. TiO_2 and 0.5 wt% Pt/TiO_2 were characterized by X-ray diffraction (Phillips APD3700 X-ray diffractometer equipped with a Cu K_α radiation source giving a wavelength of 1.5406 A) and UV-Vis spectroscopy UV-Visible spectrophotometer (HITACHI U-3010) equipped with a Praying Mantis diffuse reflectance accessory.

Photocatalytic Degradation of Methylene Blue in an Aqueous Solution

Photocatalytic degradation of Methylene Blue was studied with on two different modes. The first involves a square quartz reactor containing a 50 ml aqueous solution suspending with 5

mg of the catalysts under magnetic stirring; the second involves immobilizing the TiO_2 by coating it on one side of the reactor wall by a slurry deposition technique. The concentration of MB was determined by UV-Vis spectroscopy.

In situ Infrared Study

Fig. 1 illustrates the experimental approaches used for the in situ infrared study. 50 mg of the reactant/catalyst mixture was placed in a DRIFT (diffuse reflectance) cell and then exposed to a light from Xe lamp with an intensity of 16.7 mW/cm^2. DRIFT spectrum was taken by closing the movable light collector and interrupting the photocatalytic reaction,

RESULTS AND DISCUSSION

Characterization

Figure 2 shows the XRD patterns of TiO_2, 0.5 wt% Pt/TiO_2, 1 wt% Pt/TiO_2, and 3 wt% Pt/TiO_2. XRD results shows that TiO_2 contains both anatase and rutile, confirming the P-25 structure; increasing the Pt content leads to an increase in the intensity of the Pt (111) peak at 39.8^o. The absence of Pt peak in 0.5 wt% TiO_2 suggests the Pt particle size on 0.5 wt% Pt/TiO_2 is less than 3 nm.

Figure 3 shows the results of the diffuse reflectance UV-Vis spectra of the TiO_2, 0.5 wt% Pt/TiO_2, 1 wt% Pt/TiO_2, and 3 wt% Pt/TiO_2. TiO_2 gave the absorption edge at 450 nm. The addition of Pt shifted the absorption edge to the lower wavelength and decreased the absorption. The latter could be resulted from increases in reflection from Pt metal particles.

Aqueous Phase Kinetic Study

Figure 4 shows the kinetics of MB photocatalytic degradation in an aqueous solution with suspending TiO_2 and 0.5 wt% Pt/TiO_2 particles. The rate of disappearance of MB fit well into the first order kinetics as shown in Fig. 5. This could be due to the presence of the significant excess H_2O which reduces the kinetic rate law into the pseudo first order form. The rate constant obtained from fitting, listed in Table 1, is in the same order of magnitude with those reported in literature. In general, the rate constant depends on the catalyst composition and concentration as well as the wavelength and intensity of the illuminating light. Results in Fig 4 and Table 1 show increasing the catalyst concentration increased the rate constant. The addition of Pt had little effect on the MB degradation.

Figure 5 shows the kinetics of MB degradation in an aqueous solution on TiO_2 and 0.5 wt% Pt/TiO_2 coating on the reactor wall. The objective of this study is to determine the photocatalytic oxidation kinetics in the absence of screening effect of the catalyst particles. The initial MB concentration was 30 ppm in the aqueous solution. 1.2 mg catalyst was coated on a surface of 4.5 cm^2

In situ Infrared Study

Figure 6 shows the key characteristic IR bands of MB on CaF_2, TiO_2, and 0.5wt% Pt/TiO_2. Methylene blue exhibits the aromatic ring C=C/C=N at 1599 cm^{-1}, C=C at 1488 cm^{-1}, C-H at 1388 cm^{-1}, the aromatic amine C_{Ar}-N at 1332 cm^{-1}, and the C-H wagging at 1250 cm^{-1}. The bands in 1400 – 1600 cm^{-1} became obscure for methylene blue on both TiO_2 and 0.5 wt% Pt/TiO_2 due to the strong IR absorption background of the TiO_2 catalysts. The IR bands observed in Figure 6 are summarized in Table 2. Both TiO_2 and Pt/TiO_2 exhibited a number of OH groups. These bands were attenuated after impregnating MB onto the catalysts.

Figure 7 shows the DRIFT spectra of MB on TiO_2 during photocatalytic degradation. Exposure of MB on TiO_2 to the UV illumination led to: (i) decrease in IR intensity of all the above bands as well as C-H at 2931 cm^{-1} and C=C in the aromatic ring at 1488 cm^{-1}; (ii) increase in IR intensity of the bands of C=O at 1718 cm^{-1} and N-H at 1576 cm^{-1}. The IR results suggested that MB photocatalytic oxidation proceeded the intermediates containing carbonyl functional group (C=O) and produced ammonium ion (NH^{4+}). Figure 8 shows photocatalytic degradation of MB on 0.5 wt% Pt/TiO_2. To compare the difference in the rate of change in IR intensity for both TiO_2 and 0.5 wt% Pt/TiO_2, the IR intensity of the MB bands was plotted in Figure 9. The presence of Pt accelerated the rate of decreases in the C_{Ar}-N band at 1332 cm^{-1} and increased the rate of formation of the N-H band at 1576 cm^{-1}.

CONCLUSIONS

Pt has been shown to be effective in promoting photocatalytic reactions. This study shows that Pt promotes photocatalytic oxidation of MB on TiO_2. However, the presence of the aqueous phase diminishes the Pt effect. The high rate of photocatalytic oxidation suggests that the electron and hole separation do take place at an appreciable rate. The low rate of photocatalytic reduction reaction process can not be attributed to the low efficiency of electron and hole separation. The low rate of photocatalytic reduction process could be due to lack of the site to transfer of electron and hole to the desirable adsorbed species.

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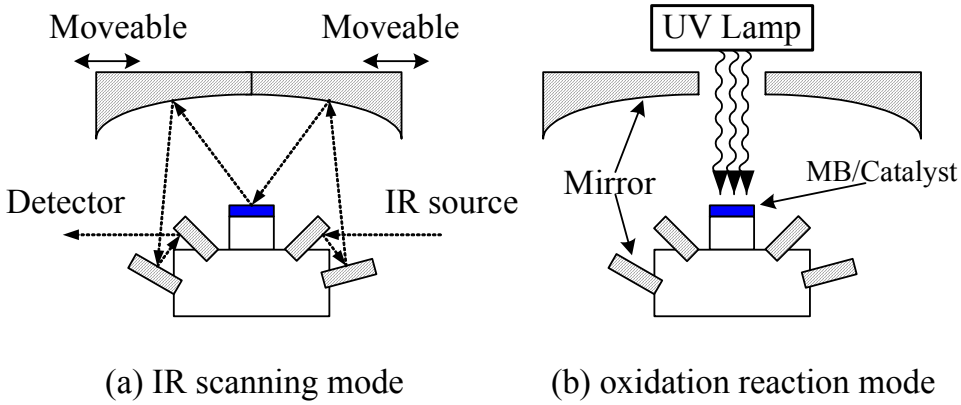

Fig. 1. Schematic diagrams of MB photocatalytic oxidation on Diffuse Reflectance Infrared Fourier Transform Spectroscopy reactor.

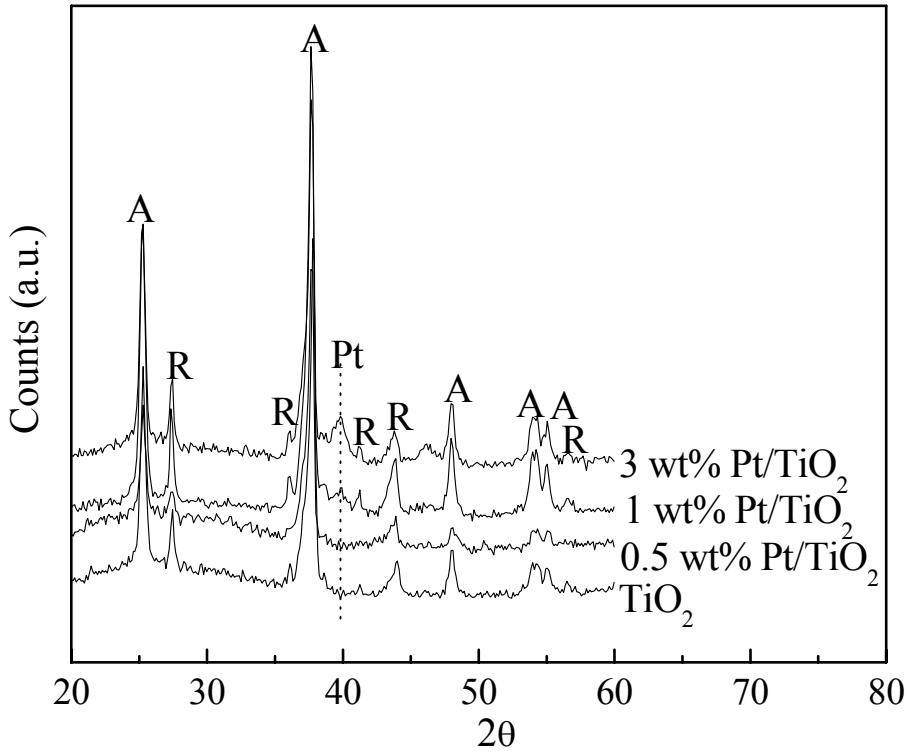

Fig. 2. XRD patterns of pure TiO_2, 0.5 wt% Pt/TiO_2, 1 wt% Pt/TiO_2 and 3 wt% Pt/TiO_2. A and R designate anatase and rutile respectively.

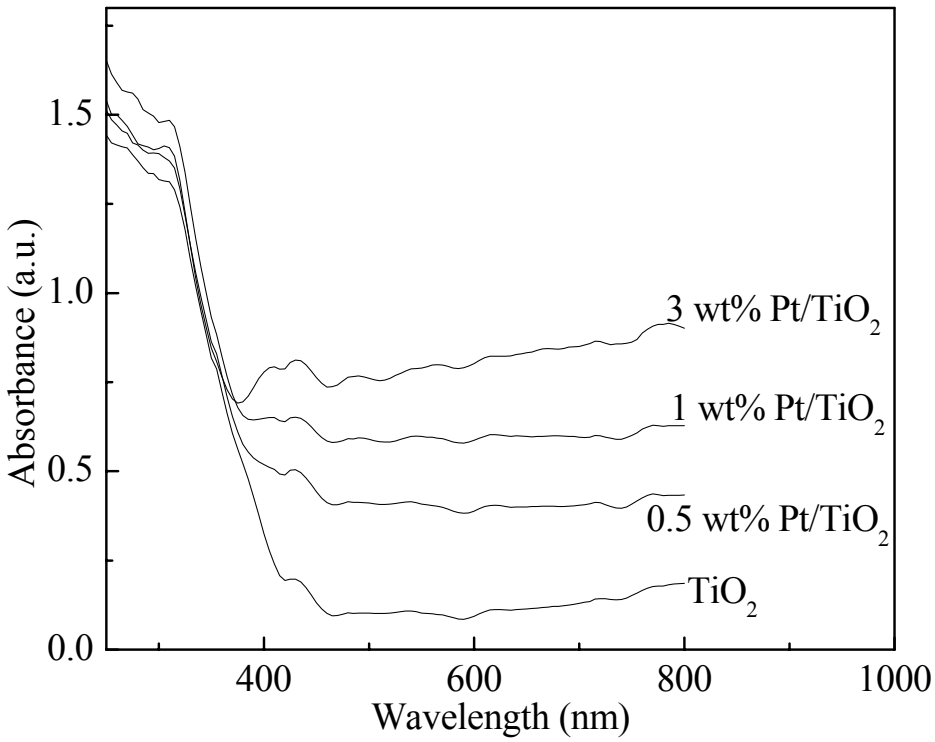

Fig. 3. UV-vis diffuse reflectance spectra of pure TiO_2, 0.5 wt% Pt/TiO_2, 1 wt% Pt/TiO_2 and 3 wt% Pt/TiO_2.

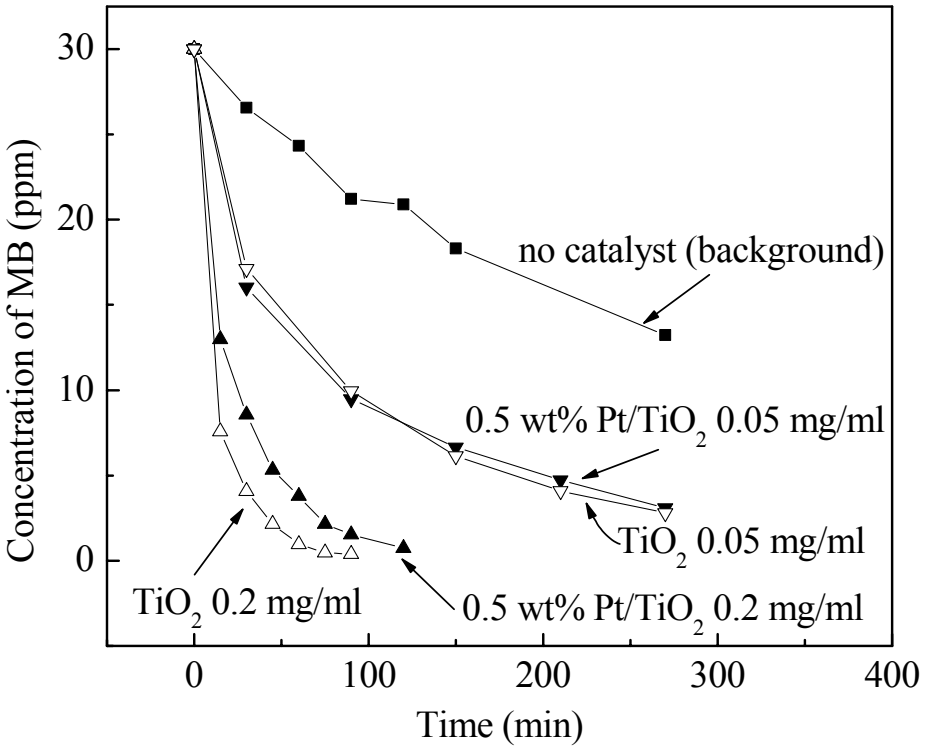

Fig. 4. Concentrations of MB as a function of time in photocatalytic oxidations of MB in aqueous solution with non-catalyst, pure TiO_2,

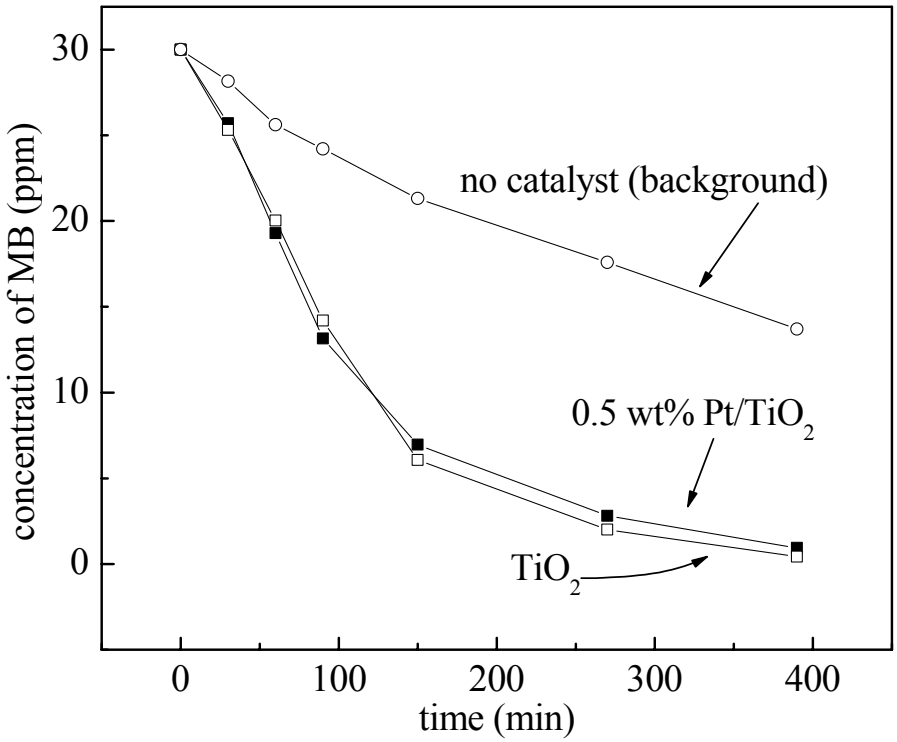

Fig. 5. Photocatalytic oxidation of MB in liquid-thin film system with non-catalvst. P25. and 0.5 wt% Pt/P25.

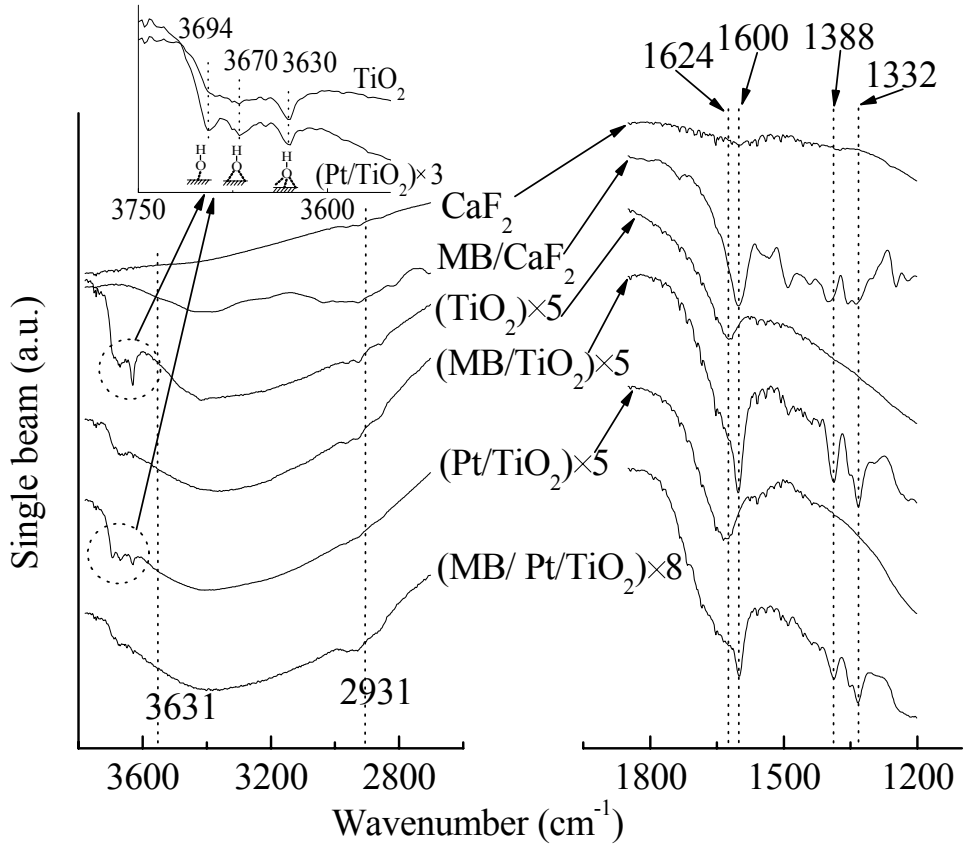

Fig. 6. IR backgrounds of CaF_2 and MB/CaF_2, TiO_2 and MB/TiO_2, 0.5 wt% Pt/TiO_2 and MB/ 0.5 wt% Pt/TiO_2. The insert shows the different types of isolated hydroxyl group over TiO_2 and 0.5 wt% Pt/TiO_2 surfaces. × indicates the spectrum is enlarged by a certain factor.

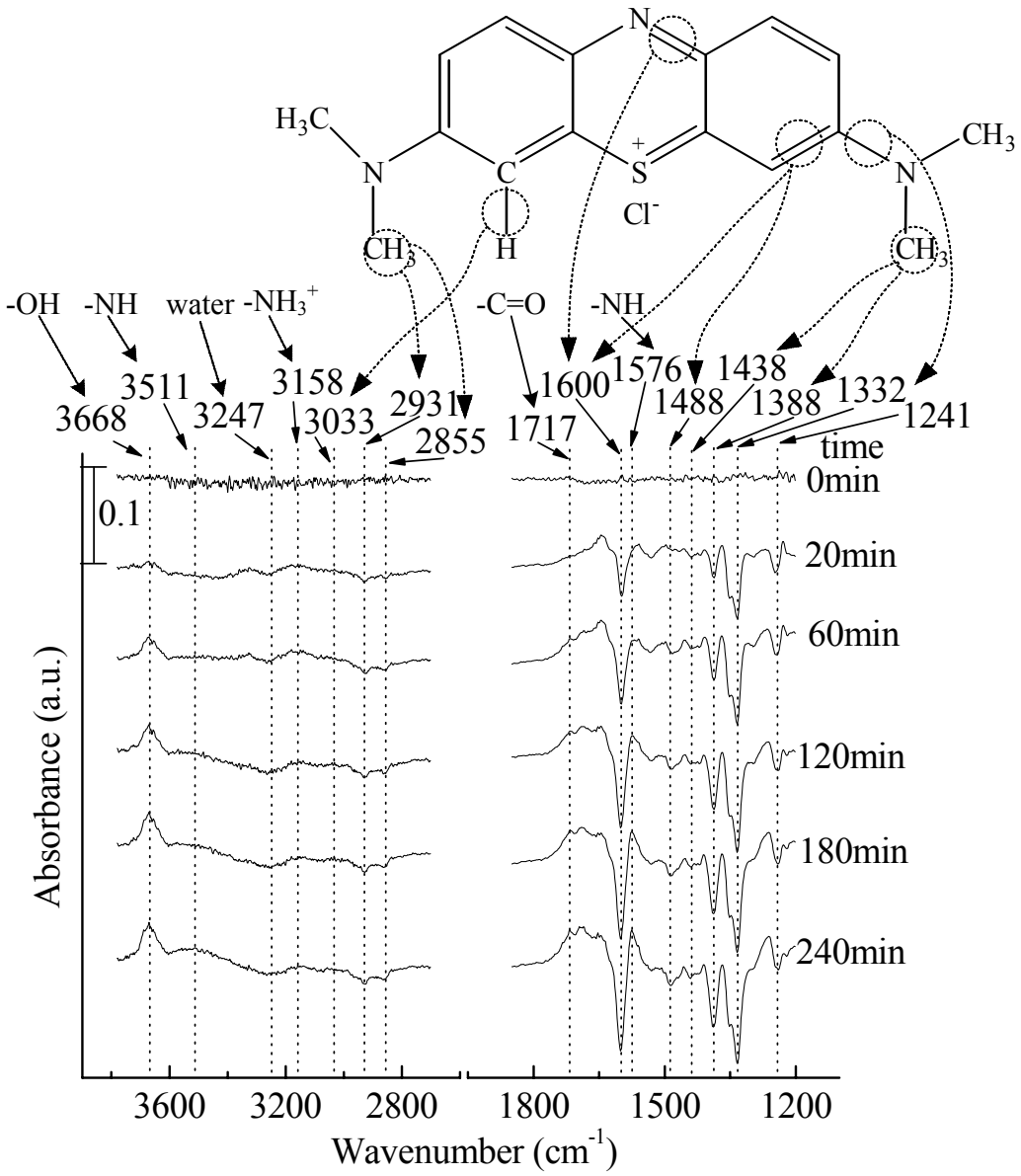

Fig. 7. In situ DRIFTS spectra and band assignments of MB photocatalytic oxidation over pure TiO_2 with 5 wt% MB at 1 atm

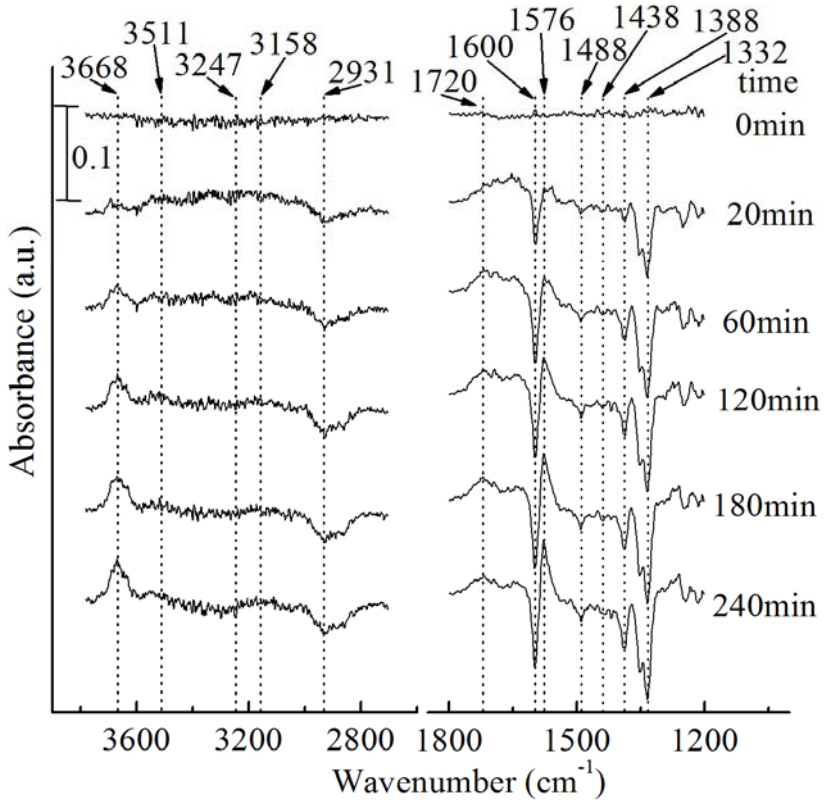

Fig. 8. In situ DRIFTS spectra of MB photocatalytic oxidation over 0.5 wt% Pt/TiO_2 with 5 wt% MB at 1 atm and 25 ºC.

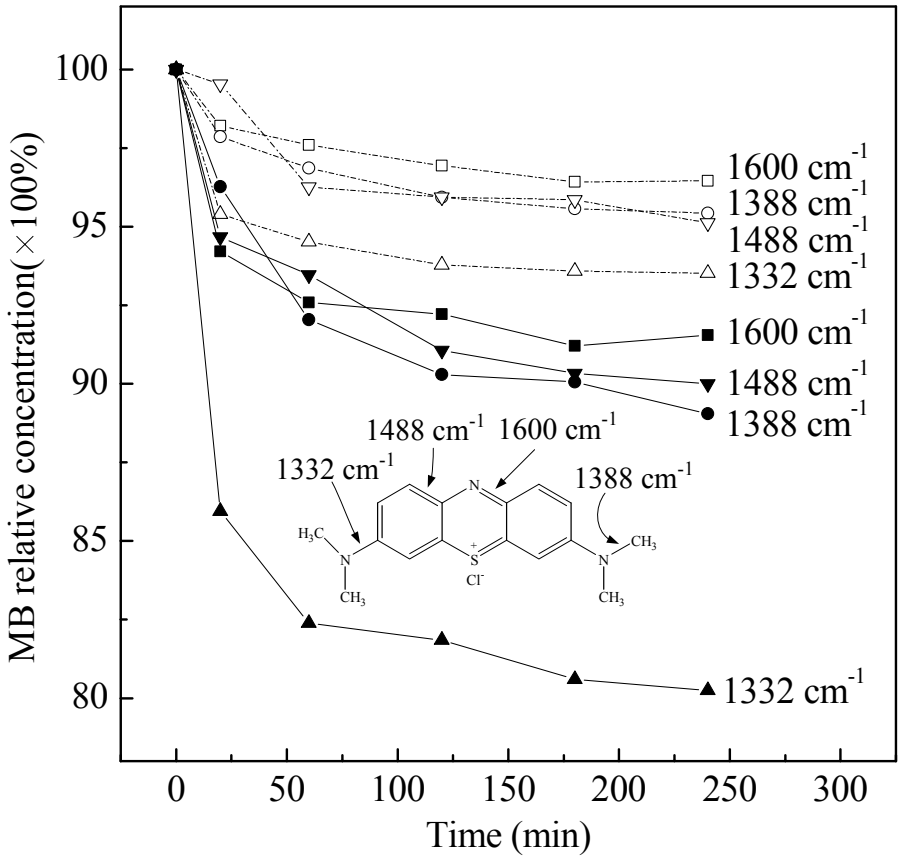

Fig. 9. Decrease rates of MB characteristic bands as a function of time in the MB photocatalytic oxidation over pure TiO_2 (dash line and empty symbol) and 0.5 wt% Pt/TiO_2 (black line and solid symbol) with 5 wt% MB at 1 atm and 25 ºC.

Table 1: literature review for MB photocatalytic oxidation in aqueous solution

catalyst	Reaction conditions: C_{MB0}, C_{cat}, I	Kinetics model and reaction constant, k	reference
P25 (30nm)	C_{MB0}=93.8 µmol/l C_{ca}t=0.2 g/l I=16.7mW/cm^2	first-order kinetics k=0.048 min^{-1}	This paper
P25 (30nm)	C_{MB0}=100 µmol/l C_{ca}t=2 g/l I=4.7mW/cm^2	first-order kinetics k=0.032 min^{-1}	1
P25 (30nm)	C_0=84.2 µmol/l C_{cat}=0.5 g/l I= N/A	first-order kinetics k=0.053 min^{-1}	2
P25 (30nm)	C_0=25 µmol/l C_{cat}=2 g/l I: N/A	first-order kinetics k=0.078 min^{-1}	3
P25 (30nm)	C_0=6.6 µmol/l C_{cat}=0.67 g/l I: N/A	first-order kinetics k=0.0288 min^{-1}	4
TiO_2 (50 nm)	C_0=20 µmol/l C_{cat}=0.218 g/l I=N/A	first-order kinetics k=0.004 min^{-1}	5
TiO_2 (20 nm)	C_0=31.3 µmol/l C_{cat}=1 g/l I=N/A	first-order kinetics k=0.025 min^{-1}	6
TiO_2 (29.5 nm)	C_0=39.1 µmol/l C_{cat}=1.2 g/l I=N/A	first-order kinetics k=0.0188 min^{-1}	7
TiO_2 (20 nm)	C_0=46.9 µmol/l C_{cat}=1.2 g/l I=N/A	first-order kinetics k=0.0672 min^{-1}	8
0.75 wt% Pt/TiO_2 (40-80 nm)	C_0=46.9 µmol/l C_{cat}=1.2 g/l I=N/A	first-order kinetics k=0.1042 min^{-1}	8
TiO_2 (18.3 nm)	C_0=62.6 µmol/l C_{cat}=1.2 g/l I=N/A	first-order kinetics k=0.0955 min^{-1}	9
0.5 wt% Au/TiO_2 (11.8-14.2nm)	C_0=62.6 µmol/l C_{cat}=1.2 g/l I=N/A	first-order kinetics k=0.1752 min^{-1}	9
TiO_2 (18.3 nm)	C_0=37.5 µmol/l C_{cat}=1.2 g/l I=N/A	first-order kinetics k=0.0144 min^{-1}	10
0.5 wt% Au/TiO_2 (19.4 nm)	C_0=37.5 µmol/l C_{cat}=1.2 g/l I=N/A	first-order kinetics k=0.052 min^{-1}	10

C_{MB0}: initial concentration of MB in solution.

C_{cat}: concentration of catalyst in reaction solution.

I: light intensity.

Table 2: assignment of the FTIR bands observed in MB photocatalytic oxidation over TiO_2 at 1 atm and 25 ºC.

Frequency (cm^{-1})	Vibration mode of functional group
3668	-OH
3511	-NH
3247	Absorbed water
3158	$-NH_3^+$
3033	Aromatic C-H
2931	$-CH_3$ asymmetric stretching
2855	$-CH_3$ symmetric stretching
1718	-C=O
1600	C=N/C=C
1576	-N-H
1488	C=C
1438	$-CH_3$ asymmetric deformation
1388	$-CH_3$ symmetric deformation
1333	Aromatic amines, C_{Ar}-N