Effect of RuO_2 deposition on the activity of TiO_2: Photocatalytic oxidation of trichloroethylene in aqueous phase

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The deposition of transition metal/metal oxide on TiO_2 to modify the surface of TiO_2, in order to improve its photocatalytic activity, is an area of great concern. Such surface modification has most often resulted in increased photocatalytic activity of TiO_2, especially in aqueous phase reactions [1–4]. This has been rationalized to be due to the ability of these transition metal deposits to inhibit the electron–hole recombination process of semiconductors during photocatalysis [1–4]. It is well documented that this recombination process is an impediment to enhanced reaction rates and also a major energy-wasting step [1, 2, 4]. The metallization of TiO_2 using transition metal deposits remains as one of the most promising approaches that can be employed to reduce the electron–hole recombination process. Pd and most especially Pt are the best candidates as metal deposits because they have shown striking improvement of the photocatalytic activity of TiO_2 [1, 4]. The use of precious metals (Pt or Pd) for TiO_2 metallization may prove uneconomical because of the difficulty associated with the recyclability of powdered catalysts used in wastewater treatment. Therefore, there is a need to explore other effective ways of metallizing TiO_2 with other non-precious metals such as RuO_2.

RuO_2 is an efficient hole and electron transfer catalyst on TiO_2 and seems to improve the efficiency of charge separation at the metal oxide/semiconductor interface, when deposited in small amounts, because an excess amount is capable of acting as a recombination center [1]. An important beneficial effect of RuO_2 loading on TiO_2 is the increase in conductivity, which ultimately allows more efficient charge transfer within the photocatalyst and makes it kinetically faster when it is involved in redox processes [5]. Most studies carried out so far on photocatalytic oxidation reactions with TiO_2/RuO_2 involve either H_2O cleavage reactions or reactions in which hydrogen is evolved. To the best of our knowledge the use of TiO_2/RuO_2 as catalyst in aqueous phase photocatalytic oxidation reactions involving chloro-hydrocarbons has not been reported. In this work, materials belonging to TiO_2-RuO_2 system have been prepared by impregnation and slurry precipitation using Degussa P-25 TiO_2 (P-25) and TiO_2 glass fiber cloth (TiO_2-GFC) as supports. An evaluation of their photocatalytic activities during trichloroethylene (TCE) oxidation in aqueous phase has been carried out. A correlation between their photocatalytic activities and the method employed for RuO_2 deposition has been established. The activity of TiO_2-GFC/RuO_2 has also been compared with those of TiO_2-GFC/Pt and TiO_2-GFC/Pt/RuO_2.

P-25 (non porous, mainly anatase, 50 m^2g^{-1}) was provided by Nippon Aerosil, Japan, while TiO_2-GFC (dimension = 5.5 cm × 10 cm; amount of TiO_2 loaded = 4.8 mg/cm^2) was supplied by Nippon Muki Co. Ltd., Japan. TiO_2-GFC has been characterized in detail by Murabayashi *et al.* [6]. P-25/RuO_2 was prepared by impregnation [7] and slurry precipitation [2] using $RuCl_3 \cdot 3H_2O$ (Aldrich) as RuO_2 precursor. The sequential deposition of Pt and RuO_2 on TiO_2-GFC in the bifunctional photocatalyst was performed by photoplatinization [8] using $H_2PtCl_6 \cdot 6H_2O$ (Wako Chemicals) as the Pt precursor and impregnation (mentioned above, [7]) respectively.

Photocatalytic oxidation reaction of TCE (reagent grade; purchased from Junsei Chemical Co., Ltd., Japan) was executed in a batch reactor, consisting of a 'test-tube' Pyrex vessel of 400 ml with a three-necked teflon-lid with gas-in, gas-out and sample port at 298 K. The gas-in and gas-out openings were closed throughout the reaction. 300 ml aqueous solution containing 5 mg/l of TCE was prepared by stirring the neat compound with deionized water for more than 6 h. The experiment was performed under continuous magnetic agitation by placing the glass fiber cloth sample vertically in the solution or mixing 0.05 g of the powdered sample with the solution. The batch reactor was completely sealed to minimize the escape of TCE due to volatilization. Illumination in the near UV (300–440 nm) was carried out by eight black light lamps (8 × 20 W, Toshiba FL20S.BLB, intensity = 3.2 mW/cm^2) positioned at a distance of 7 cm from the batch reactor. Before and during illumination, 2 ml of the sample was withdrawn from the batch reactor at regular intervals and TCE present was extracted with 3 ml of n-hexane and analyzed with a Hitachi G5000 gas chromatograph equipped with an electron capture detector.

The deposition of RuO_2 on P-25 by impregnation slightly improved the photocatalytic activity of P-25 as presented in Fig. 1. The photocatalytic activity is expressed in terms of the rate of TCE oxidation. This slight improvement in activity was observed between 0.1 and 0.3 wt%. The initial increase in activity after the deposition of 0.1 wt% of RuO_2 was higher than subsequent increases in activity on addition of more RuO_2. This result also reveals that the deposition of RuO_2 by slurry precipitation deactivated P-25. P-25 (0 wt% RuO_2) subjected to the process of slurry precipitation

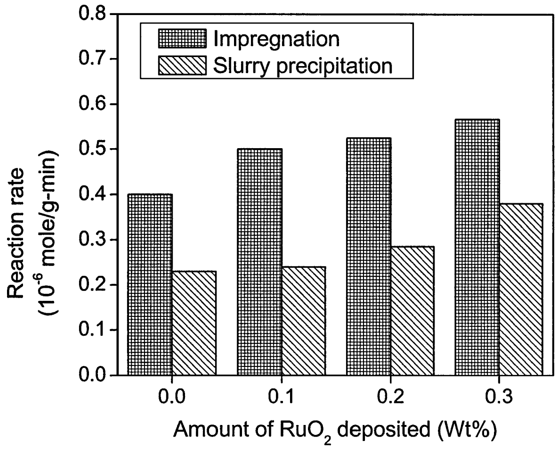

Figure 1 Comparison of the photocatalytic activities of P-25/RuO_2 prepared by slurry precipitation and impregnation methods. TCE = 5 mg/L, UV light = 3.2 mW/cm^2, P-25 = 0.05 g.

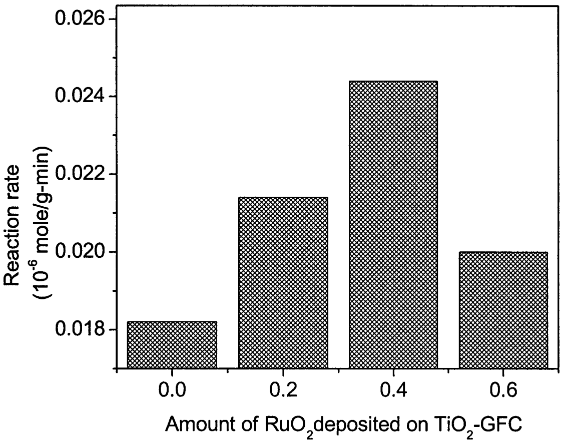

Figure 2 Average reaction rate of TCE photocatalytic degradation in aqueous-phase as a function of the amount of RuO_2 deposited on TiO_2-GFC. TCE = 5 mg/L, UV light = 3.2 mW/cm^2, P-25 = 0.05 g.

without $RuCl_3 \cdot 3H_2O$ showed activity lower than native P-25. However, the activity of P-25 (0 wt%) subjected to the process of impregnation without $RuCl_3 \cdot 3H_2O$ was similar to native P-25. Crittenden *et al.* [9] have shown that the high photocatalytic activity of P-25 is not enhanced by platinization. The slight improvement in activity of P-25/RuO_2 observed between 0 and 0.3 wt% is therefore significant.

Due to the deactivating effect of the process of slurry precipitation observed with P-25/RuO_2 samples (Fig. 1), RuO_2 was deposited on TiO_2-GFC using the impregnation method. An increase in photocatalytic activity was observed between 0 and 0.4 wt% of RuO_2 on TiO_2-GFC as presented in Fig. 2. The increase in photocatalytic activity observed for TiO_2-GFC was over ten times higher than that of P-25/RuO_2. The decrease in activity of TiO_2-GFC beyond 0.4 wt% suggests that the optimum amount of RuO_2 deposition on TiO_2-GFC is $\sim$0.4 wt%. According to Sakata *et al.* [1] when RuO_2 particles are deposited very densely on the surface of TiO_2 (in our case $> \sim 0.4$ wt%), the RuO_2 particles can function as recombination centers because the distance between particles becomes shorter than the distance in which the image force to both electrons and holes is effective. Also, the presence of excess RuO_2 deposits on TiO_2-GFC may shield the surface of TiO_2-GFC from UV light illumination and this prevents the activation of TiO_2.

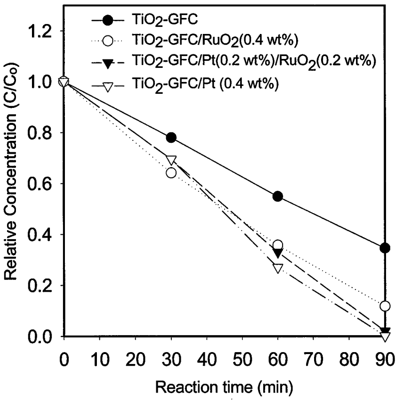

Figure 3 Photocatalytic degradation of TCE in aqueous phase using TiO_2-GFC, TiO_2-GFC/RuO_2, TiO_2-GFC/Pt and TiO_2-GFC/Pt/RuO_2. TCE = 5 mg/L, UV light = 3.2 mW/cm^2, P-25 = 0.05 g.

Comparisons of the photocatalytic activities of TiO_2-GFC, TiO_2-GFC/RuO_2, TiO_2-GFC/Pt and a bifunctional photocatalyst (TiO_2-GFC/Pt/RuO_2) have been carried out as presented in Fig. 3. The photocatalytic activity is based on the consumption of TCE expressed in normalized concentrations with time. The photocatalytic activities of TiO_2/Pt and TiO_2/RuO_2 with 0.4 wt% of Pt and RuO_2 deposits within 60 min of the reaction were almost indistinguishable. The calculated half-life values were approximately the same. Platinized TiO_2-GFC, however, showed a slightly higher activity than TiO_2-GFC/RuO_2 after 90 min. The activity shown by TiO_2-GFC/RuO_2 was greater than that of TiO_2-GFC.

The sequential deposition of both RuO_2 and Pt on TiO_2-GFC in the bifunctional photocatalyst was performed with the aim of substituting half the amount of Pt in platinized TiO_2 while maintaining its high photocatalytic activity. The substitution of 0.2 wt% of Pt in TiO_2-GFC/Pt with RuO_2 did not result in a significant decrease in photocatalytic activity as evidenced by the complete consumption of TCE after 90 min using either TiO_2-GFC/Pt or TiO_2-GFC/Pt/RuO_2 as presented in Fig. 3.

This work shows that a non-precious metal oxide catalyst (RuO_2) can be used effectively to accomplish enhanced photocatalytic activity of TiO_2 in aqueous phase. From the above results, it is concluded that the photocatalytic activity of TiO_2/RuO_2 is dependent on the method employed for preparation. Slight improvement in the activity of P-25 has been accomplished through the deposition of RuO_2 on P-25 by impregnation. This method is therefore recommended for the preparation of efficient TiO_2/RuO_2.

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