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Comparison of Photocatalytic Performance of Degussa TiO_2 P25 and P90 in Gas Phase Photocatalytic Reactor

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Photocatalytic performances of Degussa TiO_2 P25, one of the most active commercial photocatalysts and P90, recently developed material by Degussa, were studied using gas phase photocatalytic reactor. Photodecomposition of methyl *tert*-butyl ether was used to characterize photocatalytic behaviour of two samples containing different ratio of TiO_2 anatase and rutile. This is the first demonstration that although the activity of P90 was higher than that of P25 TiO_2, the surface area normalized activity showed that P25 had a better performance.

Key Words: Photocatalysis, TiO_2, P25, P90, Titania, Methyl *tert*-butyl ether.

INTRODUCTION

In the past decades, hundreds of reports have been published on TiO_2-mediated destruction of organic pollutants and volatile organic compounds (VOCs)[1]. Methyl *tert*-butyl ether (MTBE) is VOC of a significant concern, which originates from gasoline spills. It can cause significant irritation of eyes and lungs, especially at high concentrations. Photocatalysis is a promising way to eliminate MTBE from the environment. Titania (TiO_2) has been used as the most promising photocatalyst due to its high activity and stability. TiO_2 exists mainly in two polymorphs, anatase and rutile, with the most active sample often containing both crystal structures.

It is known that the ratio of anatase to rutile can have a significant effect on photocatalytic activity[2]. Moreover, the synergetic effects of the mixed-phase TiO_2 can play a significant beneficial role[3,4]. For example, Yu *et al.*,[3] reported that the composite of two kinds of semiconductors (*e.g.*, anatase-brookite or anatase-rutile) is advantageous in reducing the recombination of photo-generated electrons and holes resulting in enhancing photocatalytic activity[4].

Degussa TiO_2 P25 is a nanoparticulate titania powder (typically containing 80:20 ratio of anatase/rutile), which is widely recognised as the benchmark material for photocatalytic studies. P25 is produced through the high temperature (< 1200 ºC) flame hydrolysis of $TiCl_4$ in the presence of hydrogen and oxygen. Afterwards the TiO_2 is treated with steam to remove HCl, which is also produced as part of the reaction[5]. P90 is a new commercial catalyst comprising of smaller diameter nanoparticles of mainly anatase structure (> 90 %)[6]. It is produced using a procedure analogous to that of P25. Only few studies have been conducted on P90[7,8].

The degradation of organic pollutants, such as methyl *tert*-butyl ether (MTBE), is a very important topic in environmental protection area. Photocatalytic degradation of gas phase methyl *tert*-butyl ether has been investigated with respect to the byproducts produced and the associated mechanisms by Park *et al.*[9]. As far as the mechanism of degradation is concerned, attack by generated hydroxyl radicals on the methoxy group in the MTBE structure dominated and preceded through producing *tert*-butyl formate (TBF) as an intermediate. *Tert*-butyl formate finally degrades to CO_2 through acetone, which is easily converted to CO_2[9].

In this study, photocatalytic behaviour of different ratio of anatase/rutile content in TiO_2 was characterized by using the gas/solid, single pass photocatalytic reactor. The novel aspects of this work are related to comparison of the photocatalytic activity of P25, one of the most active commercial catalysts and P90, recently developed material by Degussa. The role of such physico-chemical parameters as surface area in photocatalytic activity is also discussed.

EXPERIMENTAL

We acknowledge the Degussa Company contribution in providing P25 and P90 photocatalysts. Methyl *tert*-butyl ether (100 ppm) gas cylinder was purchased from BOC.

System: The photochemical oxidation of MTBE was studied in the setup shown in Fig. 1. This continuous flow system was used to perform photocatalytic degradation of gaseous organic compounds over modified and unmodified TiO_2 under UV-vis light. Reactor inlet and effluent samples were analyzed with Shimadzu gas chromatograph.

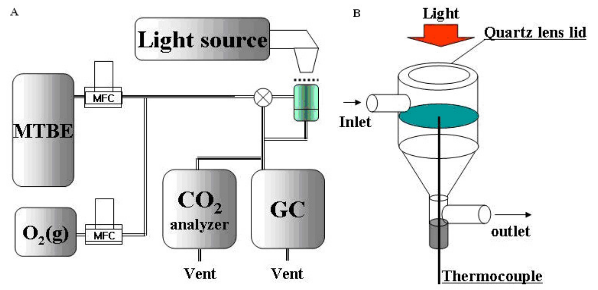

Fig. 1. (A) Schematic diagram and photograph of the gas/solid, single pass photocatalytic reactor and analysis system. (B) Schematic diagram and photograph of the gas phase photocatalytic reactor

The gas/solid, single pass photocatalytic reactor is shown in Fig. 1b. The lamp was placed over the reactor, which was 13.2 cm in length and 3.6 cm inner diameter. The total volume of the reactor was 114 mL with illuminated volume of the photocatalytic reactor being 87 mL).

The reactor incorporates 2 ports and a screw type lid: the first port is for the inlet of reactant gas and the second port for the outlet of reaction products. The reactor also included a thermocouple for the measurements of sample temperature. The reactor window was made of quarts lens, which were transparent in the UV-vis region. A separate experiment, which involved placing a heating band inside the reactor, was used to account for thermal effects during the reaction.

The catalyst (100 mg) was supported on a glass frit (I.D. 36 mm). Methyl *tert*-butyl ether vapour (68 ppm) and oxygen were supplied to the reactor at a total flow-rate of 44 mL min^{-1} (space velocity *ca.* 4,400 h^{-1}). The temperature of the illuminated samples was measured by an embedded thermocouple. A thin catalyst bed was used to minimise any gradients in temperature and light absorption (test temperature = 22 ºC).

In this work, the reaction system consisted of 1000 W Xe lamp (light intensity is 50 ± 5 mW/cm^2) and optical filters that transmit the radiation with wavelength above either 320 or 420 nm (Andover Corporation optical filters 320FG01-50 and 420FG03-50).

Since photolysis reactions are shown to occur in the region below 300 nm, this design effectively eliminated the photolysis contribution towards the photocatalytic degradation of organic species. The flux was collimated by a condenser, then filtered to reduce the IR component of the irradiant flux and afterwards is passed through a long wavelength filter to eliminate radiation below either 320 or 420 nm. To allow compensation for lamp aging an optoelectronic system, which stabilizes the output, was used. The system consisted of a photodiode and two cut-off filters to allow the selection of the UV-vis region, a neutral density filter and electronic components for signal processing and display. By changing the operating voltage of the lamp power supply, a stable output was achieved.

Sample analysis: Quantitative detection of reactants and products was achieved using a Shimadzu GC-14B gas chromatograph (J & W capillary column, DB-1, 60 mm × 0.530 mm, 5.00 µm, 100 % dimethylpolysiloxane) equipped with a flame ionization detector (FID). CO_2 production was monitored by a non-dispersive infrared spectrometry (SIEMENS ULTRAMAT-6). XRD of powder samples was done using Philips PW1820 diffractometer with copper (Cu) source (2θ from 20-80º, 0.015º step size and 1.0 s per step). The "Powder Cell v. 2.3 (Federal Institute for Materials Research and Testing, Berlin, Germany)" program was used to analyze the X-ray patterns. The ratio of the two different crystal forms was calculated according to the peak intensity ratio of $I_A(101)/I_R(110)$. The Brunauer-Emmett-Teller (BET) surface area was determined using a Micromeritics Gemini 2360 Analyser. UV-Vis diffuse reflectance spectra of the powder samples were obtained using a PerkinElmer UV-vis spectrometer (λ 12) with Labsphere RSA-PE-20 (a diffuse reflectance and transmittance accessory).

RESULTS AND DISCUSSION

The focus of this study is to identify the major differences between the two different types of TiO_2 photocatalysts (*i.e.*, P25 and P90), by quantitatively comparing their photocatalytic activities. All experiments were carried out under identical experimental conditions. The insert in Fig. 2 shows XRD patterns of the as-received P25 and P90 powders. X-Ray diffraction analysis of P25 and P90 materials showed that both materials consist of TiO_2 anatase and rutile phases. The anatase contents are 80 and 90 % for P25 and P90, respectively.

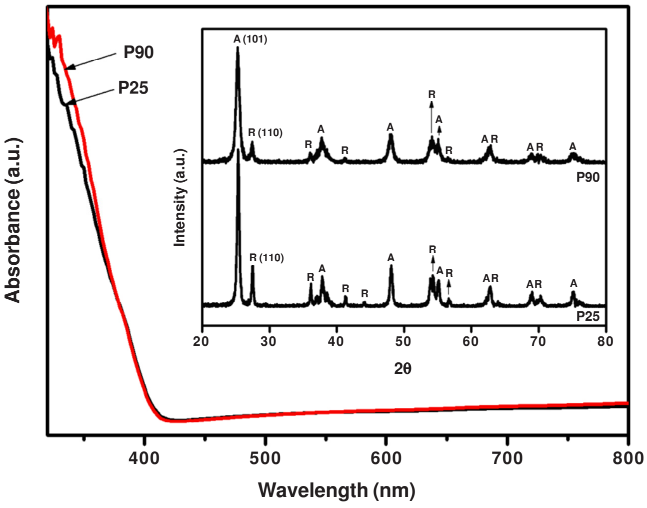

Fig. 2. UV-Vis diffuse reflectance spectra of P25 and P90. UV-Vis spectra of P25 and P90 were almost identical. Inset shows X-ray diffraction (XRD) patterns for P25 and P90 (A, anatase; R, rutile)

The Brunauer-Emmett-Teller (BET) surface areas, crystal structures and mean crystallite sizes for P25 and P90 catalysts are summarized in Table-1(A). The crystal sizes of anatase crystallite were 24 and 14 nm for P25 and P90, respectively. The sample surface areas were 100.4 and 57.4 m^2 g^{-1} for P90 and P25, respectively. The surface area increase was consistent with the particle size decrease[10].

TABLE-1

(A) Properties of P25 and P90

	S_{BET} ($m^2 g^{-1}$)	Phase	Mean crystallite size (nm)
P25	57.4	Anatase:rutile/80:20	24
P90	100.4	Anatase:rutile/90:10	14

(B) Photocatalytic decomposition of MTBE before and after normalisation for BET surface area

	Conversion (%)	Normalized conversion (% $m^2 g^{-1}$)
P25	61.1	1.06
P90	72.0	0.72

Fig. 2 shows the corresponding UV-vis diffuse reflectance spectra of P25 and P90. Even though P90 sample contained more anatase than P25 did, the UV-vis spectra did not reflect this difference, it is possible that UV-vis spectrometer was not sensitive enough to detect the spectral shift. There was no optical absorption in the visible region, indicating that both P25 and P90 are inactive under visible radiation.

The photocatalytic decomposition of MTBE by P25 and P90 under ultraviolet and visible light irradiation was studied in the gas/solid, single pass photocatalytic reactor. Both of P25 and P90 did not show significant photocatalytic activity in the visible region, as expected. The conversions of MTBE with P25 and P90 under UV light irradiation were 61.1 and 72.0 %, respectively. Oxygen scavenging experiments by Durrant *et al.*[7] showed a similar trend. The results may be attributed to the fact that P90 has a larger surface area and smaller crystallite size.

Fig. 3 shows CO_2 production monitored during the photocatalytic test under UV light irradiation. For P90 and P25 the CO_2 concentrations were 82 and 72 ppm, respectively. It is evident that the CO_2 generation and MTBE conversions were considerably higher for P90 as compared to those of P25, consistent with the higher surface area of P90.

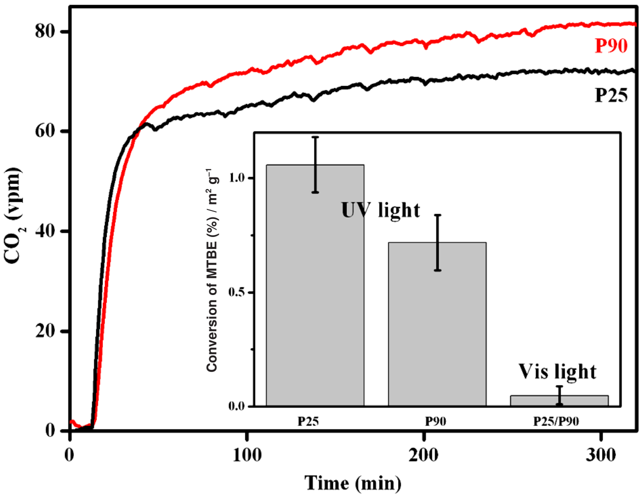

Fig. 3. CO_2 analysis of the photocatalytic destruction of MTBE using P25 and P90 under UV light irradiation. Inset shows photocatalytic activity of P25 and P90 normalised for BET surface area. When the results were normalized with BET surface area, P25 showed higher activity than that of P90

However, when the results were normalized with BET surface area, P25 showed higher activity than that of P90. Table-1(B) and the insert in Fig. 3 show photocatalytic activity of P25 and P90 normalized for BET surface area. The normalized conversion of P25 is 0.34 %/$m^2 g^{-1}$ higher than that of P90. The increased presence of rutile phase and synergetic effects of rutile and anatase may be responsible for the increased photocatalytic activity[2] of P25. In the mixed-phase TiO_2 it has been proposed that the exited electrons selectively migrate to either rutile[11] or anatase[12], leading to excess holes in the other phase. This separation slows electron/hole recombination and the phase with excess holes is presumably more reactive, leading to greater photocatalytic activity[13].

Small quantities of intermediate products have been detected. In the case of P90 catalyst these amounted to 24.2, 0.8 and 1.2 % of MTBE consumed for *t*-butyl formate, acetone and acetaldehyde, respectively. For P25 catalyst these amounted to 22.7, 0.8 and 1.1 % of MTBE consumed for *t*-butyl formate, acetone and acetaldehyde, respectively.

Conclusion

A comparison of the photocatalytic activity of P25, one of the most active commercial catalysts and P90, recently developed material by Degussa was conducted. For this study a gas/solid catalysis experimental system was designed and built. This system allowed control of methyl *tert*-butyl ether (MTBE) concentration up to a few ppm and maintained steady state gas flow rate.

The photocatalytic activity of P90 under UV radiation was considerably higher than that of P25, consistent with the higher surface area of P90. However, the surface area normalized activity showed the opposite trend, where P25 had the highest activity, while both catalysts being essentially inactive in the visible region.

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