



Effect of microwave radiation on the (Raman) lattice phonons in selected titanium dioxide solid specimens

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ABSTRACT

The effects of 2.45-GHz microwave radiation on the Raman-active lattice phonons of two selected (Wako) anatase and rutile specimens and on Degussa P-25 TiO₂ nanoparticles were probed by *in situ* microscopic Raman spectroscopy in the solid phase with samples subjected to microwave irradiation (MW) or in combination with UV illumination (UV/MW). Significant changes were seen in the Raman band intensities for the pure anatase E_g mode at 143 cm⁻¹ and for the rutile vibration at 446 cm⁻¹, whereas only negligible changes in intensity were observed for the 144 cm⁻¹ band of P-25 nanoparticles exposed to MW and UV/MW radiation. It is deduced that microwaves have a negligible impact on the lattice vibrational modes (phonons) of P-25 titania, even though this specimen was thermally heated by the microwaves. The photodegradation of phenol was re-visited to examine the photoactivity of the TiO₂ specimens selected for the *in situ* Raman study, as attested by the number of •OH radicals produced (DMPO spin trap ESR) under UV versus UV/MW irradiations, and by the related enhanced dynamics under UV/MW irradiation relative to UV alone or UV/CH.

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1. Introduction

Literature of the past two decades has demonstrated convincingly the advantages of microwaves in syntheses, as the reaction times are shortened considerably from days to several minutes, often with significantly improved product yields. A continuing debate in microwave chemistry concerns whether microwaves are simply a source of heat (the thermal effect) or whether the microwaves impart some additional effects on the reaction components (the non-thermal effect or sometimes referred to as the specific effect) that also impact on the reaction dynamics [1–3]. In this regard, a study in phase transfer catalysis in solvent-free media, which showed significant differences in reaction dynamics between conventional and microwave heating, led Stuerger and Gaillard [4] to suggest that a very small density of superheated areas (i.e. hot spots) in the system was sufficient to induce a consequent rate enhancement, and that the lack of intrinsic stirring in inorganic

solids (e.g. alumina, silica and clays) precludes a uniform distribution of microwave-generated heat by thermal diffusion. Along similar lines, Tsukahara et al. [5] inferred non-equilibrium local heating of dimethylsulfoxide (DMSO) molecules in proximity of Co metallic particles that was induced only by microwave irradiation of the heterogeneous solid–liquid system and not by conventional heating. Such non-equilibrium local heating originates from a faster input of microwave energy relative to slower heat loss induced by thermal gradients between heated micro-domains and surrounding cooler domains.

During the past decade many of our studies in microwave chemistry have attempted to probe the existence of and to delineate the non-thermal effect from the thermal effect in organic syntheses and in TiO₂ photoassisted processes. In the latter case, the photoactivity of various TiO₂ materials from different sources and different compositions in aqueous dispersions improved significantly on simultaneous irradiation with 2.45-GHz microwaves and UV light [2], a phenomenon not encountered by conventional heating at identical temperature. The microwave specific effect was displayed only by the Degussa P-25 TiO₂ specimen [3], which when exposed to 2.45-GHz microwaves the photoactivity was also enhanced in comparison to irradiation with the higher frequency 5.8-GHz microwaves under identical temperature conditions [6].

Earlier we reported the effects of 2.45-GHz microwaves on the Raman lattice phonons of N-doped Degussa P-25 TiO₂ and N-doped

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Ishihara ST-01 TiO₂ samples [7]. Microwave irradiation of the ST-01 and N-doped N-ST01 TiO₂ samples displayed significant changes in the 144-cm⁻¹ optical phonons. Results of the Raman study with the 785-nm laser excitation wavelength inferred a microwave thermal effect on the Ishihara ST-01 and N-ST01 specimens, whereas for the Degussa P-25 samples the microwaves also imparted a specific effect as the microwaves influenced the N-dopant sites in contrast to the ST-01 systems where the dopant sites seemed unaffected as inferred from the temperature–time profiles.

Herein, we examine further the possible existence of a microwave (specific) effect on selected TiO₂ materials (i.e. anatase, rutile, and P-25 TiO₂) using the *in situ* Raman spectroscopic method during irradiation of the samples by 2.45-GHz microwaves (MW) and by simultaneous irradiation with both microwaves and UV radiation (UV/MW) employing a combined microscopic Raman laser (excitation laser line, 532 nm) spectrometer and an assembled microwave applicator. We further probe the photoactivity of all three commercially available materials by re-visiting the degradation dynamics of phenol in aqueous media under UV, UV/MW and UV/CH irradiation conditions. The relation (or lack thereof) between Raman spectral band intensity (lattice optical phonons), photoactivity, and the number of •OH radicals (ESR) produced is examined.

2. Experimental setup

2.1. Microwave- and photo-induced degradation of phenol

The P-25 titanium dioxide specimen was supplied by Degussa, whereas commercial anatase and rutile titanium dioxide specimens were obtained from Wako Pure Chemicals Co. Ltd. (Japan). Some of the characteristic features (e.g. content of anatase, particle sizes, BET specific surface areas, band gaps) of these materials were described previously [3].

An aqueous dispersion of phenol (0.10 mM, 30 mL, initial pH = 5.2) and TiO₂ particles (loading, 60 mg) was placed in a 150-mL Pyrex glass batch-type cylindrical reactor {Taiatsu Techno Co.; size, 160 mm (H) × 37 mm (i.d.)} located in the microwave waveguide (see Figure 1 of Ref. [3]). For these experiments, continuous microwave irradiation was obtained from a Hitachi Kyowa Engineering Co. Ltd. 2.45-GHz microwave generator (maximal power, 800 W) equipped with a power controller, a power monitor, and an isolator (air cooling device). The 60-W continuous microwaves emitted from the magnetron were measured using a power monitor. The reactor was sealed with two Byton O-rings and a stainless steel cap. A pressure gauge and a release bulb were connected to the cover of the reactor.

Unless noted otherwise, temperatures of the phenol/TiO₂ dispersions were measured using an Anritsu Meter Co., Ltd. FL-2000 fiber optic thermometer; dispersion temperature reached 112 °C maximum after 13 min under microwave irradiation, and remained constant thereafter to within the 109–112 °C range. The UV source (Toshiba 75-W Hg lamp; irradiance, ca. 0.5 mW cm⁻²; maximal emission, 360 nm) was located so as to irradiate the sample reactor through the hole on the side of the microwave waveguide. The dispersion was continually stirred during irradiation. The photodegradation of phenol was probed following three different routes: (a) UV-driven photodegradation (UV); (b) UV-driven and microwave-assisted photodegradation (UV/MW); (c) UV-driven photodegradation with conventional heating (UV/CH) at temperatures otherwise identical to those under UV/MW irradiation. In the UV/CH case, a segment of the cylindrical Pyrex reactor was coated with a metallic film using the metal–organic chemical vapour deposition (MOCVD) technique on one side at the bottom of the reactor to provide the external heat source; applied voltage to the metal-

lic film was <100 V. The uncoated side of the reactor was used to allow the UV light through. The rate of increase of temperature by the UV/MW route was continually monitored during the irradiation period; the applied voltage on the metallic film was then varied to obtain a heating rate for the UV/CH method identical to that of the UV/MW method. That is, the quantity of thermal energy supplied to the photoreactor contents at each irradiation time was the same for both the UV/MW and UV/CH routes. The dynamics of the process were monitored by the loss of UV absorption features of phenol recorded with a JASCO liquid chromatograph (HPLC) equipped with a JASCO UV-2070 UV–vis diode array, a multi-wavelength detector, and a JASCO Crestpak C-18S column. The eluent consisted of a methanol/water solution (1:2, v/v ratio). The relative number of •OH radicals photogenerated in UV- and microwave-irradiated TiO₂ aqueous suspensions was determined relative to a Mn²⁺ standard by DMPO spin-trap ESR spectroscopy (DMPO, 5,5-dimethyl-1-pyrrolidine-N-oxide) by a procedure reported earlier [3,8]. Experimental limitations precluded assessing the relative number of •OH radicals produced under the UV/CH conditions (see, e.g. Ref. [8] for a schematic of the equipment).

2.2. *In situ* observation of Raman spectra

The laser Raman microscopic system was a JASCO Co. system (NRS-5100) integrated into an assembled microwave irradiation applicator (see, e.g. Figure 2 of Ref. [3]). The TiO₂ powdered samples (loading, 0.1 mg) were placed on the microwave irradiation copper dish (ϕ = 8 mm) of the microwave applicator (width, 34 mm; depth, 37 mm; height, 20 mm). Continuous microwave radiation was obtained from a 2.45-GHz microwave semiconductor generator (Fuji Electronic Industrial Co. Ltd.; GNU-201AA; maximal power, 200 W) through a BNC (Bayonet–Neil–Concelman) cable. The applied microwave power was 35.2 W and the reflected microwave power was 0.2 W; the actual microwave applied power was likely less than 30 W owing to possible losses of microwaves in the BNC cable. Microwave radiation incident on the TiO₂ powder on the copper dish was monitored with a 2.45-GHz microwave leak detector (Fuji Electronic Industrial Co. Ltd.). Raman spectra were recorded through a hole (ϕ = 7.8 mm) in the microwave apparatus.

Temperature changes of the TiO₂ powder were monitored with a radiation thermometer. The *in situ* observation of Raman spectra was carried out under microwave irradiation in the dark (MW/dark) and under simultaneous microwave and UV radiations (UV/MW). The incident UV light originated from a fluorescent lamp (irradiance, ca. 0.3 μ W cm⁻² at 360 nm) through the hole on the lid of the microwave applicator. Specimens were UV-irradiated continuously up to 1500 s (i.e. 25 min). The Raman spectra were recorded at 30-s intervals between 0 and 1500 s using the 532-nm laser excitation wavelength. In exploratory experiments we determined an error margin of 2.2% in the peak intensities of the Raman bands for the TiO₂ specimens in the absence of MW and UV irradiation.

3. Results and discussion

3.1. Nature of the P-25 TiO₂

The P-25 TiO₂ consists mostly of well interwoven anatase (ca. 70–80%) and rutile (ca. 20–30%) crystallite forms, depending on the batch, and has been shown to be highly photoactive in photoreductive and photooxidative processes. Details of the microstructure of this photocatalyst are relevant in understanding the photophysical and/or photochemical processes that could limit its efficiency, and that of other titania materials. Bickley et al. [9] suggested that the enhanced photoactivity of P-25 TiO₂ was due to a layer of rutile covering the surface of individual anatase particles that led to a

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