



Sonochemical water splitting in the presence of powdered metal oxides



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ABSTRACT

Kinetics of hydrogen formation was explored as a new chemical dosimeter allowing probing the sonochemical activity of argon-saturated water in the presence of micro- and nano-sized metal oxide particles exhibiting catalytic properties (ThO_2 , ZrO_2 , and TiO_2). It was shown that the conventional sonochemical dosimeter based on H_2O_2 formation is hardly applicable in such systems due to catalytic degradation of H_2O_2 at oxide surface. The study of H_2 generation revealed that at low-frequency ultrasound (20 kHz) the sonochemical water splitting is greatly improved for all studied metal oxides. The highest efficiency is observed for relatively large micrometric particles of ThO_2 which is assigned to ultrasonically-driven particle fragmentation accompanied by mechanochemical water molecule splitting. The nanosized metal oxides do not exhibit particle size reduction under ultrasonic treatment but nevertheless yield higher quantities of H_2 . The enhancement of sonochemical water splitting in this case is most probably resulting from better bubble nucleation in heterogeneous systems. At high-frequency ultrasound (362 kHz), the effect of metal oxide particles results in a combination of nucleation and ultrasound attenuation. In contrast to 20 kHz, micrometric particles slowdown the sonolysis of water at 362 kHz due to stronger attenuation of ultrasonic waves while smaller particles show a relatively weak and various directional effects.

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1. Introduction

Power ultrasound is frequently applied for dispersion of powdered solids in order to enhance the kinetics of heterogeneous solid/liquid processes [1]. Along with this mechanical effect, the chemical transformations triggered with ultrasound are also known for a long time [2]. While homogeneous sonochemistry originates from extreme and transient conditions produced in the gas phase of cavitation bubbles [3], heterogeneous sonochemistry also depends on numerous secondary effects of acoustic cavitation, such as acoustic streaming, jetting, splashing, shock waves and shearing forces [4]. Quantification of heterogeneous sonochemistry is an important task for the optimization of ultrasonically-driven dissolution, synthesis of nanostructured materials, and sonocatalysis. The latter process based on the joint action of heterogeneous catalysts and ultrasonic waves has been found to be an attractive advanced technology for the elimination of organic contaminants from wastewater [5–7]. For some systems, the synergetic effect of ultrasound and catalysts has been reported [8,9]. Hydrogen peroxide and molecular hydrogen are well known to be formed as principal products of homolytic splitting of water molecules inside

the collapsing bubbles. Usually, the formation of hydrogen peroxide during water sonolysis is applied to probe the chemical efficiency of cavitation [10]. Several studies reported the enhancement of sonochemical H_2O_2 production in aqueous suspensions of TiO_2 , quartz, glass beads and Al_2O_3 compared to pure water [11–14]. However, the origin of such phenomenon remains to be better understood, even if many authors associate the beneficial effect of particles to the enhancement of bubble nucleation due to crevices, entrapped gas or impurities on particle surfaces, surface stabilization of the bubble by nanoparticles at the interface, or improvement of the surface reactivity of particles due to the effect of bubble collapse. It should be noted that H_2O_2 reacts with numerous oxide surfaces via catalytic decomposition and, therefore, the kinetics of its sonochemical formation can be strongly impacted by the presence of solid particles [15].

This work is focused on the kinetics of hydrogen formation during sonolysis of water in the presence of powdered metal oxides. In contrast to H_2O_2 , using H_2 as a probe of sonochemical activity allows to minimize the secondary processes related for instance to reactivity and typical for H_2O_2 . Several nanometric and micrometric metal dioxides (TiO_2 , ZrO_2 and ThO_2) were studied in argon-saturated water submitted to low- (20 kHz) and high-frequency (362 kHz) ultrasound in order to evaluate the effect of chemical nature as well as the particle size of these catalytically

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active metal oxides towards the sonochemical reactivity at different ultrasonic frequencies.

2. Materials and methods

2.1. Materials

All experiments were performed using deionized milli-Q water (18.2 M Ω cm). Argon (99.999% purity) was provided by Air Liquide. The crystal lattice, specific surface area (S_{BET}), particle size and morphology of metal oxides used in the experiments are summarized in Table 1. ZrO_2 and TiO_2 (A, B) oxides were purchased from Alfa Aesar and from U.S. Research Nanomaterials, Inc respectively. ThO_2 -A and ThO_2 -B were prepared following the routine oxalate precipitation/calcination protocols [16]. The samples were only differing by their calcination procedure used to reach the desired surface area: ThO_2 -A was calcinated 10 h at 1000 °C and ThO_2 -B was calcinated 10 h at 650 °C. Nanometric ThO_2 -C was obtained by precipitation of Th(IV) hydroxide with ammonia in the presence of PEG ($M = 3000$, 2.5 wt.%) followed by calcination of solids at 450 °C for 2 h in the presence of air as it was reported for the preparation of nanocrystallized ceria [17].

2.2. Reactor setup and procedure

Two kinds of ultrasonic equipment were used in this study. The experiments at 20 kHz were performed in a thermostatically controlled closed batch reactor containing 50 mL of solution, and equipped with a 1 cm² irradiating surface area titanium probe powered by a 750 W Sonics generator. The probe was immersed reproducibly below the surface of the sonicated solution.

The high-frequency ultrasonic device consisted of a thermostated glass-made batch reactor mounted on top of a high-frequency piezoelectric transducer (ELAC Nautik, 25 cm²) providing 362 kHz power ultrasound and connected to a high-frequency generator with a maximum electrical power of 125 W (T & C Power Conversion, Inc). The volume of sonicated solutions was 220 mL. In addition, mechanical stirring at 250 rpm was provided during high-frequency experiments using a glass-made three-bladed propeller agitator placed reproducibly on the top of the reactor opposite the high-frequency transducer using a tight Teflon ring.

For all experiments, the solutions were sparged with argon about 1 h before sonication and during the ultrasonic treatment at a controlled rate of 90 mL·min⁻¹. The temperature during sonolysis was maintained at 22 °C with a Huber Unistat Tango thermostat for both devices and measured by a thermocouple immersed into irradiated solution. The acoustic power density, P_{ac} (W·mL⁻¹), transmitted to the solution, was measured using a conventional thermal probe method [10] and was equal to 0.34

and 0.25 W·mL⁻¹ at 20 and 362 kHz, respectively. All experiments were performed with the same concentration of metal oxide powders of 4 g·L⁻¹. Water sonolysis without any powder was considered as a reference.

2.3. Analysis

Hydrogen in the outlet gas was identified using a quadrupole mass spectrometer (PROLAB 300, Thermo Fisher). The multiplexion monitoring (MIM) mode was employed to follow the evolution of H₂ during sonolysis. The yields of H₂ ($G(\text{H}_2)$, $\mu\text{mol}\cdot\text{kJ}^{-1}$) were determined after mass spectrometric data calibration with standard H₂/Ar gas mixtures (Messer). The statistical error for $G(\text{H}_2)$ values was estimated to be 10–15%. Water vapor in the outlet gas was trapped with molecular sieves (Aldrich, 3 Å) prior to mass spectrometric analyses.

Hydrogen peroxide in solutions was monitored by spectrophotometry with 0.02 M Ti(IV) in 1 M HNO₃ ($\lambda = 411$ nm, $\epsilon = 658$ cm⁻¹·M⁻¹) [18]. The statistical error for H₂O₂ formation rate was estimated to be 10%.

Low-resolution transmission electron microscopic (TEM) measurements were made with a Jeol JEM 3010 device (120 eV) equipped with a numeric camcorder. The samples were dispersed in absolute ethanol using an ultrasonic bath. One drop was then deposited on carbon-coated copper grid and dried in air prior to analysis.

Scanning electron microscopy measurements (SEM) were done with MEB QUANTA FEG 200 ESEM scanning microscope. The powder X-ray diffraction data were collected with a Bruker AXS D8 instrument (Cu-K α $\lambda = 1.5418$ Å). The specific surface area (S_{BET}) of the oxides was obtained by nitrogen adsorption–desorption at 77 K using a Micromeritics Tristar II 3020 apparatus. The samples were evacuated at 393 K overnight prior to analysis. The results were analyzed using the BET method.

3. Results and discussion

3.1. Low-frequency ultrasound

SEM images (Fig. 1) reveal an intensive fragmentation of micrometric refractive ThO_2 -A (ThO_2 -B) particles during prolonged irradiation by 20 kHz ultrasound. Roughly, the size of ThO_2 particles reduces from initially 5 μm to 0.5–1 μm after 12 h of ultrasonic treatment. On the other hand, nanometric ThO_2 -C, TiO_2 -A, B and ZrO_2 particles do not exhibit modification in size or morphology at similar conditions. Such difference can be attributed to the mechanism of interaction of cavitation bubbles with extended solid surfaces [18]. The resonance size of a bubble generated in sonicated water at 20 kHz, is approximately 150 μm . When a cavitation event occurs in the vicinity of relatively big particles or their aggregates, the bubble implodes asymmetrically by forming a high speed micro-jet of solvent directed towards the solid surfaces. Such micro-jet is known to lead to particle fragmentation. Shock waves resulting from the collapse of spherical bubbles may also be involved in these physical effects. By contrast, very small particles follow the movement of fluid surrounding the bubble and hardly perturb the collapse.

Kinetics curves of H₂O₂ formation shown in Fig. 2 clearly indicate a decrease of observed H₂O₂ formation rate in the presence of ThO_2 particles. TiO_2 and ZrO_2 particles exhibit similar behavior and not shown here. However, quite rapid H₂O₂ degradation is observed in the presence of ThO_2 under mechanical stirring even without ultrasound. In addition, H₂O₂ degradation under silent conditions was found to accelerate with the increase of ThO_2 specific surface area in agreement with kinetic curves shown in Fig. 2

Table 1
Characteristics of the metal oxides used in the study.

Metal oxide	Crystal structure	S_{BET} (m ² ·g ⁻¹)	Morphology and particle size
TiO ₂ -A	Rutile	29.0	Round-shaped ~30–50 nm
TiO ₂ -B	Anatase	71.1	Beans-like ~20 × 12 nm
ZrO ₂	Monoclinic	41.4	Round-shaped ~20 nm
ThO ₂ -A	Face-centered cubic	1.5	Square platelets ~5 μm
ThO ₂ -B	Face-centered cubic	10.2	Square platelets ~4.5 μm
ThO ₂ -C	Face-centered cubic	82.4	Round-shaped ~5 nm

Typical TEM and SEM images of these oxides are shown in Supporting information (Figs. S1–S3).

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